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APPROXIMATIONS FOR THE THERMODYNAMIC AND TRANSPORT

PROPERTIES OF HIGH-TEMPERATURE AIR

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SUMMARY

The thermodynamic and transport properties of high-temperature air are found in closed form starting from approximate partition functions for the major components in air and neglecting all minor components. The compressibility, energy, entropy, the specific heats, the speed of sound, the coefficients of viscosity and of thermal conductivity, and the Prandtl numbers for air are tabulated from 500° to 15,000° K over a range of pressure from 0.0001 to 100 atmospheres. The enthalpy of air and the mol fractions of the major components of air can easily be found from the tabulated values for compressibility and energy. It is predicted that the Prandtl number for fully ionized air will become small compared to unity, the order of 0.01, and this implies that boundary layers in such flow will be very transparent to heat flux.

INTRODUCTION

It is axiomatic that the science of aerodynamics must be based on a good understanding of the atmospheric medium through which vehicles are to fly. Under subsonic flight conditions, air may be treated as an ideal gas composed of rigid, rotating diatomic molecules. The thermodynamic properties of such a gas are well known and they are accounted for in the gas flow equations by the familiar ratio of specific heats, which in this case is a constant. Under supersonic flight conditions, air may be raised to temperatures where the molecules can no longer be treated as simple, rigid rotators. At relatively low supersonic speeds, vibrational energy is excited and then the specific heats become functions of temperature. However, both the thermodynamic and transport properties of air in vibrational excitation can be predicted with fair accuracy by the methods of quantum statistics and kinetic theory (ref. 1), and the air-flow relations can be modified accordingly. Eggers (ref. 2) has calculated the effects of vibrational energy on the one-dimensional, inviscid flow of diatomic gases, for example.

Further changes in air properties may occur at still higher flight velocity. Flight velocities of practical interest have now increased from low supersonic speeds to the escape velocity, 37,000 feet per second. Vehicles which travel at these hypervelocities excite the air to such

high temperatures that the molecules not only vibrate but may dissociate
into atoms and even ionize. Under these conditions, the behavior of air
deviates widely from that of an ideal gas and the thermodynamic and trans-
port properties all become functions of pressure as well as of tempera-
ture. It is, of course, essential to evaluate these functions in order
to calculate the pattern of air flow about high-speed vehicles, the vis-
cous and pressure forces which result, and the heat flux which occurs
between the air and the vehicle.

The equilibrium thermodynamic properties of a gas can be calculated
with great confidence, provided the energy levels of the gas particles
and the degeneracy of these levels are known. For monatomic and diatomic
gases this information can generally be deduced from spectroscopic data
with such accuracy that the calculated thermodynamic properties can be
trusted to very high temperatures, even where experimental confirmation
is lacking. In the case of air, however, one of the important energy
terms was not known with confidence until recently, namely, the dissocia-
tion energy of molecular nitrogen. This uncertainty arose because the
available spectroscopic data were consistent with two different models
for nitrogen dissociation, one leading to a dissociation energy of 7.37
electron volts per molecule and the other to 9.76 electron volts per
molecule. At first, the lower value was widely accepted as the most
probable one (Herzberg, ref. 3). Krieger and White (ref. 4) and
Hirschfelder and Curtiss (ref. 5) have published tables of thermodynamic
properties of high-temperature air based on this value. Gaydon (ref. 6)
was perhaps one of the first advocates of the view that the higher value
was the correct one. Subsequently a number of experiments were performed
which confirmed Gaydon's opinion, among them the measurements of strong
shock waves in nitrogen made by Christian, Duff, and Yarger (ref. 7) and
the detonation studies made by Kistiakowsky, Knight, and Malin (ref. 8).
This rendered the work of references 4 and 5 obsolete, but shortly there-
after Gilmore (ref. 9) computed the chemical composition, energy, entropy,
compressibility, and pressure of air as functions of temperature and den-
sity based on the higher value for the dissociation of nitrogen. Later,
Hilsenrath and Beckett (ref. 10) published a similar table of these prop-
erties, but in much smaller increments of temperature and density. The
calculations in both of these references (9 and 10) are highly refined
in the sense that they not only account for the major components of air
and their most significant energy states, but they also take into account
a large number of the higher energy states which are infrequently excited,
even at high temperatures, and most of the very minor chemical components
of air are included. Therefore these works are among the most detailed
estimates for the thermodynamic properties of air which have been made.
Also it is not likely that these works will become obsolete, since the
values of all the important energy levels used in these calculations are
now quite secure. However, it is desirable to have approximate expres-
sions for these properties in closed form which can be solved without
iteration. Such solutions would be particularly valuable, for example,
in preparing tables to be used with the method of characteristics for
calculating the flow of real air.

In contrast to the fairly satisfactory state of development in regard to thermodynamic properties, knowledge of the transport properties of air at high temperatures is in an elementary stage. It is generally agreed that an accurate calculation of the transport properties should be based on the rather rigorous theory of Chapman and Enskog for monatomic gases (ref. 11). The extension of this theory given by Wang-Chang and Uhlenbeck (ref. 12) would be used for molecular gases with internal energy. For such calculations it is necessary to know the interaction potentials which exist between the gas particles so that the so-called collision integrals can be calculated. Hirschfelder, Curtiss, and Bird (ref. 13) have developed the theory of intermolecular collisions to the stage where the collision integrals and the transport properties of inert molecular gases can be calculated with good accuracy. However, when the air dissociates, as it does at high temperatures, the atom-atom and atom-molecule potentials are needed, and these are not sufficiently well known to calculate the collision integrals. At the present time, calculation of the atom-atom and the atom-molecule potentials is being attempted by quantum mechanical methods. However, it may be some time before these solutions are available, and even when they are completed a formidable obstacle to the calculation of the transport properties remains. This occurs because two atoms may approach each other along any one of a number of potentials, depending upon the principal quantum number of the electrons and the spatial orientation of the electron spin and orbital momentum vectors at the time of collision. These potentials are quite different, some are partly attractive and others are entirely repulsive. The solutions for all of these potentials are implicit in the quantum mechanical description of the problem. It is hoped that these potentials might be weighted by their probabilities to yield single effective potentials for each species, for if the atoms which interact along each different potential must be treated as a separate species in the gas, the calculations of the transport properties will be laborious indeed, even with electronic computing. Problems of this type are further compounded when temperatures are considered where the air begins to ionize. In any event, there is an urgent need for an estimate of the properties of air, due to the demands created by the expanding realm of very high-speed flight. Therefore, an engineering approximation for the transport properties of high-temperature air would be valuable in the interim while more exact solutions are being prepared. Even after more precise solutions are available, an approximation giving the transport properties in closed form will be just as desirable as it is for the thermodynamic properties of air.

In view of the needs outlined above, it is the purpose of this paper to develop approximate expressions for the properties of air over the range of temperatures and pressures encountered by vehicles traversing the atmosphere at speeds up to escape velocity. The principle which shall be used in deriving these expressions is that they shall be made as simple in form as possible. For the thermodynamic properties this is accomplished by keeping only those terms which are necessary to yield a final result within a few percent of the more exact solutions. The properties of air which will be evaluated are the compressibility (i.e., the correction to

the ideal gas equation of state), the energy, enthalpy, entropy, specific
heat at constant pressure and at constant density, the speed of sound,
the viscosity, thermal conductivity, and the Prandtl number. All of
these properties will be evaluated for equilibrium conditions. Because
of the finite reaction rates, these values will doubtless need to be modi-
fied for processes which involve changes in state which are rapid compared
to the rate of approach to chemical equilibrium. Nonequilibrium effects
will probably be encountered in very high-altitude flight because the
approach to equilibrium is slow at the low pressures experienced there.
However, there is experimental evidence that equilibrium is essentially
realized in flow of dissociating air under conditions encountered in
flight at moderate altitudes and speeds (ref. 14). In addition,
Hirschfelder (ref. 15) has argued that heat transfer in pure conduction
processes will correspond to equilibrium values if the reaction rate in
one direction is rapid. Therefore, the thermodynamic and transport prop-
erties of air which are based on equilibrium conditions should apply
directly to some practical problems as well as being a convenient reference
for the nonequilibrium values.

SYMBOLS

a speed of sound (zero frequency)

a_i, b_i stoichiometric coefficients for components A_i and B_i

A_i, B_i components of a chemical reaction

C Sutherland's constant (eq. (58))

C_i specific heat per mol at constant density for component i

C_p specific heat per mol at constant pressure

C_p' partial specific heat per mol at constant pressure,
$$\sum_i x_i (C_i + 1)$$

C_v specific heat per mol at constant density

D dissociation energy per molecule, also diffusion coefficient

D_{ij} binary diffusion coefficient for molecules of type i into
molecules of type j

e base of natural logarithms, also electron charge

e^- electron

E	energy per mol, also electric field strength
E_i	energy per mol of component i
E_O	energy per mol at zero absolute temperature
g_i	degeneracy of the ith state
g_n	degeneracy of the nth electronic state
h	Planck's constant
H	enthalpy per mol
H_i	enthalpy per mol of component i
I	molecular moment of inertia, also ionization energy per molecule
I_O	resonance potential for ionization
J	rotational quantum number
k	Boltzmann constant, also thermal conductivity
k_O	reference coefficient of thermal conductivity (eq. (77))
k_n, k'	coefficient of thermal conductivity due to molecular collisions
k_r	coefficient of thermal conductivity due to chemical reaction
K_c	chemical equilibrium constant for concentration units
K_p	chemical equilibrium constant for pressure units
Le'	partial Lewis number, $\dfrac{D\rho C_p'}{\overline{M}k'}$
$\ln$	logarithm to the base e
m	mass of a gas particle
M_i	molecular weight per mol of component i
$\overline{M}$	mean molecular weight per mol of a gas mixture
M_O	molecular weight per mol for undissociated molecules

n   vibrational quantum number, also electronic quantum number, also concentration in moles per unit volume

$\left.\begin{array}{l} n(A_i), \\ n(B_i), \ldots \end{array}\right\}$ concentration of components A_i, B_i, ... in moles per unit volume

N   nitrogen atom, also atoms in general

N_0 Avagadro number, molecules per mol

N^+ nitrogen plus ion, also plus ions in general

N_2 nitrogen molecule

NO   nitric oxide

O   oxygen atom

O^+ oxygen plus ion

O_2 oxygen molecule

p   pressure

p_0 reference pressure, 1 atmosphere

$\left.\begin{array}{l} p(A_i), \\ p(B_i), \ldots \end{array}\right\}$ partial pressure of components A_i, B_i, ...

Pr   Prandtl number, $\dfrac{C_p \eta}{\bar{M}k}$

Pr'   partial Prandtl number, $\dfrac{C_p' \eta}{\bar{M}k'}$

Q   total partition function

Q_t translational partition function

Q_r rotational partition function

Q_v vibrational partition function

Q_e electronic partition function

Q_c total partition function for a standard state of unit concentration, $\dfrac{p}{RT} Q$

Q_p

total partition function for a standard state of unit pressure, pQ

$\left.\begin{array}{l} Q_p(A_i), \\ Q_p(B_i), \ldots \end{array}\right\}$

total partition functions for components A_i, B_i, $\ldots$

r

distance between atoms

r_e

distance between atoms where the potential is a minimum

R

universal gas constant, energy per mol deg

S

entropy per mol

S_i

entropy per mol of component i at 1 atmosphere pressure

S_o

collision cross section for undissociated air molecules

$\left.\begin{array}{l} S_{ij} \quad \text{or} \\ S(i\text{-}j) \end{array}\right\}$

collision cross section for particle i with particle j

T

absolute temperature

u_i

mean molecular velocity for molecule type i

u_o

mean molecular velocity for undissociated air molecules

U

potential energy between gas particles

x

mol fraction

x_i

mol fraction of component i

$x(A_i) \ldots$

mol fraction of component $A_i \ldots$

Z

compressibility, $\dfrac{pM_o}{\rho RT}$ or $\dfrac{M_o}{\overline{M}}$

α

molecular symmetry number (equal 2 for homonuclear diatomic molecules), also polarizability

β

Morse function constant (eq. (61))

γ

ratio of specific heats, $\dfrac{C_p}{C_v}$

ϵ

fraction of molecules which are dissociated or of atoms which are ionized

ϵ_i energy of the ith state

ϵ_n energy of the nth electronic state

ζ dimensionless distance parameter, $\dfrac{r}{r_e} - 1$

η coefficient of viscosity

η_0 reference coefficient of viscosity (eq. (67))

λ_i mean free path for molecule type i

λ_0 reference mean free path (eq. (71))

ν vibrational frequency

ρ_i density of molecule type i

ρ_0 reference density (eq. (70))

σ collision diameter

Subscripts

p   partial derivative at constant pressure

ρ partial derivative at constant density

s   partial derivative at constant entropy

i,j   indices referring to molecules type i and j

t,r,v,e   indices referring to the contribution of translational, rotational, vibrational, and electronic energy modes, respectively

THERMODYNAMIC PROPERTIES

As a preliminary, a brief review of some of the results of statistical mechanics will be given. This will include the definitions of the partition functions and will summarize those relations between these functions and the thermodynamic properties of gases which will be used in the approximations to follow.

Partition Functions

All of the thermodynamic properties of a gas may be calculated from its partition function. Consequently, the first step in determining the properties of air is to calculate the partition functions for the components in air. The partition function may be defined as

$$Q = \sum_{i=1}^{\infty} g_i e^{-\frac{\epsilon_i}{kT}} \tag{1}$$

where ϵ_i is the energy of the ith state of the gas particle and g_i is the degeneracy, that is, the number of states of the particle which have this same energy level. The energy may be due to the translational, rotational, or vibrational motion of the particle, or to the motion of the electrons within the particle. The temperatures being considered in this paper are in all cases low enough that the excited nuclear energy states may be disregarded. The usual assumption is made that no coupling exists between the different modes of energy. Then the partition function may be expressed as the product

$$Q = Q_t Q_r Q_v Q_e \tag{2a}$$

The factors on the right side of equation (2a) are, respectively, the partition functions associated with the translational, rotational, vibrational, and electronic energy levels of the gas particle. Each factor is determined independently by an equation of the same form as equation (1). By the methods of statistical mechanics it is found that for diatomic molecules these factors are:

$$Q_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{RT}{p} \tag{2b}$$

$$Q_r = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{h^2 J(J+1)}{8\pi^2 IkT}} \simeq \frac{8\pi^2 IkT}{\alpha h^2} \tag{2c}$$

$$Q_v = \sum_{n=1}^{\infty} e^{-\frac{nh\nu}{kT}} = \left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1} \tag{2d}$$

$$Q_e = \sum_{n=1}^{\infty} g_n e^{-\frac{\epsilon_n}{kT}} \tag{2e}$$

The notations used above are common ones and the derivation of the equations may be found in any standard text on statistical mechanics, such as reference 16 or 17. For monatomic particles, which have no modes of rotational or vibrational energy, the rotational and vibrational partition functions take the value unity. The translational and electronic partition functions for such particles take the same form as equations (2t and (2e), respectively.

Consistent with the stated purpose of this paper, only those exponential terms are included in the electronic partition function (eq. (2e)) for which the energy levels, ϵ_n, are less than six times kT at the maximum temperature considered ($15,000^\circ$ K). Actually, the levels are so widely split in this range that the closest to this cutoff is the sixth state of the atomic nitrogen ion, just a little more than four times kT at $15,000^\circ$ K.

Table I presents the atomic and molecular constants which were used in calculating the partition functions. The molecular constants for rotation, vibration, dissociation energy, and electronic energy levels were taken from Herzberg (ref. 3). The 9.76 electron-volt value for nitrogen dissociation is used, and it is assumed that the rotational and vibrational constants for all excited electronic states are the same as for the ground state. The atomic energy levels are taken from Moore (ref. 18). The constants have been rounded off to the nearest 0.5 percent, and the second and third electronic energy levels of atomic nitrogen have been combined since they lie within 0.5 percent of each other. The same treatment applies to the second and third electronic levels of the atomic oxygen positive ion.

The functions which are to be used directly in the calculations to follow are the logarithms of the partition functions. From the partition function constants (table I) and equations (2a) through (2e), these functions become

$$\ln Q(N_2) = \frac{7}{2} \ln T - 0.42 - \ln\left(1 - e^{-\frac{3390}{T}}\right) - \ln p \tag{3a}$$

$$\ln Q(O_2) = \frac{7}{2} \ln T + 0.11 - \ln\left(1 - e^{-\frac{2270}{T}}\right) +$$

$$\ln\left(3 + 2e^{-\frac{11390}{T}} + 2e^{-\frac{18990}{T}}\right) - \ln p \tag{3b}$$

$$\ln Q(O) = \frac{5}{2} \ln T + 0.50 + \ln \left(5 + 3e^{-\frac{228}{T}} + e^{-\frac{326}{T}} + \right.$$

$$\left. 5e^{-\frac{22800}{T}} + e^{-\frac{48600}{T}} \right) - \ln p \qquad (3c)$$

$$\ln Q(N) = \frac{5}{2} \ln T + 0.30 + \ln \left(4 + 10e^{-\frac{27700}{T}} + 6e^{-\frac{41500}{T}} \right) - \ln p \qquad (3d)$$

$$\ln Q(O^+) = \frac{5}{2} \ln T + 0.50 + \ln \left(4 + 10^{-\frac{38600}{T}} + 6e^{-\frac{58200}{T}} \right) - \ln p \qquad (3e)$$

$$\ln Q(N^+) = \frac{5}{2} \ln T + 0.30 + \ln \left(1 + 3e^{-\frac{70.6}{T}} + 5e^{-\frac{188.9}{T}} + \right.$$

$$\left. 5e^{-\frac{22000}{T}} + e^{-\frac{47000}{T}} + 5e^{-\frac{67900}{T}} \right) - \ln p \qquad (3f)$$

$$\ln Q(e^-) = \frac{5}{2} \ln T - 14.24 - \ln p \qquad (3g)$$

where T is the temperature in degrees Kelvin and p is given in atmospheres.

It will be surmised that those components of air which are not represented by partition functions above are to be neglected in the approximations which are to follow. The absence of a partition function for nitric oxide may be found surprising, but it will be seen later that, to the order of accuracy being considered here, the formation of nitric oxide may be neglected in computing thermodynamic properties over a wide range of pressure and temperature conditions, including those conditions which will generally be encountered in high-speed flight through the atmosphere. This occurs because NO has about the same thermodynamic properties as an average for nitrogen and oxygen molecules, and the NO

formation does not greatly influence the equilibrium mol fractions of
molecules and of atoms. The possible influence of nitric oxide on the
transport properties of air will be considered later.

Energy, Enthalpy, and Specific Heats for the
Components of Air

According to statistical mechanics, the energy and enthalpy per mol
of pure gas are given by the following relations

$$\frac{E-E_0}{RT} = T\left(\frac{\partial \ln Q}{\partial T}\right)_\rho = T\frac{d \ln Q_c}{dT} \tag{4}$$

$$\frac{H-E_0}{RT} = T\left(\frac{\partial \ln Q}{\partial T}\right)_p = T\frac{d \ln Q_p}{dT} \tag{5}$$

The quantities Q_c and Q_p are the partition functions for the standard
states of unit concentration and of unit pressure, respectively. These
are related to the total partition function by

$$Q_c = \frac{p}{RT} Q \tag{6a}$$

$$Q_p = pQ \tag{6b}$$

and they are functions only of temperature so that it is their total
derivatives which are related to the energy and enthalpy as given in
equations (4) and (5). The quantity E_0 is a constant representing the
energy of the gas at zero absolute temperature. The choice of this level
is arbitrary, but by convention E_0 is taken as zero for the molecules
of nitrogen and oxygen. Then E_0 for the neutral atoms is just one half
the energy of dissociation per mol of diatomic molecules, and E_0 for
the ionized atoms is the sum of this dissociation energy and the energy
of ionization. With all the ionization energy attributed to the ionized
atoms, E_0 for the electrons must be taken as zero, of course.

By definition the specific heats per mol of pure gas are

$$C_v = \left(\frac{\partial E}{\partial T}\right)_\rho \tag{7}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{8}$$

From equations (2a), (2b), (2e), (4), and (5) it is seen that the energy and enthalpy per mol of gas due to translation and electronic excitation are given by

$$\left(\frac{E-E_0}{RT}\right)_{t+e} = \frac{3}{2} + \frac{\sum \frac{\epsilon_n}{kT} g_n e^{-\frac{\epsilon_n}{kT}}}{\sum g_n e^{-\frac{\epsilon_n}{kT}}} \tag{9}$$

$$\left(\frac{H-E_0}{RT}\right)_{t+e} = \left(\frac{E-E_0}{RT}\right)_{t+e} + 1 \tag{10}$$

and the specific heats given by equations (7) and (8) can be expressed

$$\left(\frac{C_v}{R}\right)_{t+e} = \frac{3}{2} + \frac{\sum \left(\frac{\epsilon_n}{kT}\right)^2 g_n e^{-\frac{\epsilon_n}{kT}}}{\sum g_n e^{-\frac{\epsilon_n}{kT}}} - \left(\frac{\sum \frac{\epsilon_n}{kT} g_n e^{-\frac{\epsilon_n}{kT}}}{\sum g_n e^{-\frac{\epsilon_n}{kT}}}\right)^2 \tag{11}$$

$$\left(\frac{C_p}{R}\right)_{t+e} = \left(\frac{C_v}{R}\right)_{t+e} + 1 \tag{12}$$

Equations (9), (10), (11), and (12) give that part of the energy, enthalpy, and the specific heats which is due to the translational and electronic energy for either atoms or molecules. The contributions of rotational and vibrational energy must also be included for the molecular case, of course. According to equations (2c) and (2d) the expression

$$\left(\frac{E}{RT}\right)_{r+v} = 1 + \frac{h\nu}{kT}\left(e^{\frac{h\nu}{kT}} - 1\right)^{-1} \tag{13}$$

should be added to equations (9) and (10) in order to obtain the total energy and enthalpy for diatomic molecules, while

$$\left(\frac{C}{R}\right)_{r+v} = 1 + \left(\frac{h\nu}{2kT}\right)^2 \left(\sinh \frac{h\nu}{2kT}\right)^{-2} \tag{14}$$

should be added to equations (11) and (12) to get the total specific heats for these particles.

The entropy of a pure gas is related to its partition function by

$$\frac{S}{R} = \ln Q + T \left(\frac{\partial \ln Q}{\partial T}\right)_p \tag{15}$$

and from equations (5) and (6b), the entropy of the gas at unit pressure may be expressed

$$\frac{S}{R} = \ln Q_p + \frac{H - E_0}{RT} \tag{16}$$

The calculated values of the partition functions for a standard state of 1 atmosphere pressure, the energy, and the specific heat at constant density for the major components of air are given in table II in 500° K increments of temperature. The concentration standardized partition functions, the enthalpy, entropy, and the specific heat at constant pressure are not listed since they may be easily found from the properties tabulated and equations (6), (10), (12), and (16). The tabulated properties for each component are given for the range in temperature in which the component exists in air, at pressures between 0.0001 and 100 atmospheres, up to the maximum temperature considered, 15,000° K. We shall now examine how these values may be used in computing the thermodynamic properties of air.

Equilibrium Constants

In order to determine the equilibrium mol fractions for the components of air, it will be necessary to calculate the equilibrium constants for the chemical reactions which occur. These chemical reactions may be expressed in the general form

$$\sum a_i A_i \rightleftarrows \sum b_i B_i \tag{17}$$

where the A_i are the reactants, the B_i the products, and a_i and b_i are their respective stoichiometric coefficients. The pressure equilibrium constant for this reaction is defined in terms of the partial pressures

$$K_p = \frac{\Pi p^{b_i}(B_i)}{\Pi p^{a_i}(A_i)} \qquad (18)$$

and it is related to the partition functions by (see ref. 16)

$$\ln K_p = -\frac{\Delta E_0}{RT} + \sum b_i \ln Q_p(B_i) - \sum a_i \ln Q_p(A_i) \qquad (19)$$

where

$$\Delta E_0 \equiv \sum b_i E_0(B_i) - \sum a_i E_0(A_i)$$

is the zero point energy of the products less the zero point energy of the reactants, both referred to their standard states. The reactions considered here are the dissociation of molecular oxygen and of molecular nitrogen and the ionization of atomic oxygen and of atomic nitrogen. According to equation (19) and the partition function constants given in table I, the equilibrium constants for these reactions are

$$\ln K_p(O_2 \rightarrow 2O) = -\frac{59,000}{T} + 2 \ln Q_p(O) - \ln Q_p(O_2) \qquad (20a)$$

$$\ln K_p(N_2 \rightarrow 2N) = -\frac{113,200}{T} + 2 \ln Q_p(N) - \ln Q_p(N_2) \qquad (20b)$$

$$\ln K_p(O \rightarrow O^+ + e^-) = -\frac{158,000}{T} + \ln Q_p(O^+) + \ln Q_p(e^-) - \ln Q_p(O) \qquad (20c)$$

$$\ln K_p(N \rightarrow N^+ + e^-) = -\frac{168,800}{T} + \ln Q_p(N^+) + \ln Q_p(e^-) - \ln Q_p(N) \qquad (20d)$$

The concentration equilibrium constant is defined by

$$K_c = \frac{\Pi n^{b_i}(B_i)}{\Pi n^{a_i}(A_i)} \qquad (21)$$

where $n(A_i)$ and $n(B_i)$ are, respectively, the concentrations of the chemical reactants and products. This quantity will also be needed for subsequent calculations, and it is obtained by replacing the pressure

standardized partition functions, Q_p, with the corresponding concentration standardized partition functions, Q_c (eq. (19)). From equation (6) it is seen that

$$K_c = K_p(RT)^{\Sigma a_i - \Sigma b_i} \tag{22}$$

The logarithmic derivatives of the equilibrium constants will also be required later. From equations (5), (10), and (19) these become

$$T \frac{d \ln K_c}{dT} = \frac{\Delta E_0}{T} + \sum \left(\frac{E-E_0}{RT}\right)_{B_i} - \sum \left(\frac{E-E_0}{RT}\right)_{A_i} \tag{23}$$

$$T \frac{d \ln K_p}{dT} = T \frac{d \ln K_c}{dT} + \sum b_i - \sum a_i \tag{24}$$

The equilibrium constants and their logarithmic derivatives for the reactions represented by equations (20a) through (20d) are listed as functions of temperature in table III. These quantities will now be used in calculating the component mol fractions and their derivatives.

Calculation of the Equilibrium Mol Fractions
and Their Derivatives

The possibility that approximate solutions in closed form could be obtained for the properties of air suggests itself upon examination of the results of Gilmore (ref. 9). His tables of the composition of air show that there are four chemical reactions of major importance. These are the dissociation of molecular oxygen and of molecular nitrogen, and the ionization of atomic oxygen and of atomic nitrogen.

$$O_2 \rightarrow 2\,O \tag{25a}$$

$$N_2 \rightarrow 2N \tag{25b}$$

$$O \rightarrow O^+ + e^- \tag{25c}$$

$$N \rightarrow N^+ + e^- \tag{25d}$$

With one exception, all other reactions which occur yield component concentrations which are the order of 0.1 percent, or less, of the major components given by the reactions above. The exception is the formation

of nitric oxide, NO, which at sea level density may become as much as 10 percent of the air around 5000° K (see ref. 9). However, even this much nitric oxide does not strongly influence the resulting thermodynamic properties of air, and at densities less than 0.01 normal sea level density, where the NO is less than 1 percent, the effects are very small.

Two distinctive features of the chemical reactions given above are observable from Gilmore's results. The first is that at all pressures the dissociation of oxygen is essentially complete before the dissociation of nitrogen begins. This means that these two reactions can be treated independently for the purposes of our approximation. The second feature is that nitrogen and oxygen atoms ionize at about the same temperature and with about the same energy changes. (Note, e.g., the approximate equality of the equilibrium constants for the two ionization reactions, table III.) Consequently, it is possible to assume that once air is completely dissociated, all atoms constitute a single species which has the population weighted average properties of the nitrogen and oxygen atoms. Then the problem conveniently divides itself into three cases, and in each case only three components of the air need to be considered simultaneously. These three cases are described as follows, where the ratio of nitrogen to oxygen has been taken as 4 to 1.

Case I.- At relatively low temperatures, the three components of air which may exist simultaneously are molecular nitrogen, molecular oxygen, and atomic oxygen. If ϵ is the fraction of the initial number of moles per unit volume which have become dissociated, then the partial pressures for these three components may be expressed

$$p(N_2) = x(N_2)p = \frac{0.8}{1+\epsilon} p \qquad (26a)$$

$$p(O_2) = x(O_2)p = \frac{0.2-\epsilon}{1+\epsilon} p \qquad (26b)$$

$$p(O) = x(O)p = \frac{2\epsilon}{1+\epsilon} p \qquad (26c)$$

where the $x(A_i)$ are the mol fractions of component A_i. It is assumed that the gas components each behave like an ideal gas. Then the equation of state is

$$\frac{p}{\rho} = \frac{ZRT}{M_O} \qquad (27)$$

where the compressibility Z is $1 + \epsilon$ in this case. This quantity Z is the total number of moles per initial mol of undissociated air. It is also equal to the ratio of the initial molecular weight of undissociated air to the mean molecular weight, $M_O/\bar{M}$.

The equilibrium constant for the oxygen dissociation reaction is

$$K_p(O_2 \rightarrow 2O) = \frac{p^2(O)}{p(O_2)} = \frac{4\epsilon^2 p}{(1+\epsilon)(0.2-\epsilon)} \qquad (28)$$

Then the fraction ϵ is found by solving the quadratic equation (28)

$$\epsilon = \frac{-0.8 + \sqrt{0.64 + 0.8\left(1+\frac{4p}{K_p}\right)}}{2\left(1+\frac{4p}{K_p}\right)} \qquad (29)$$

The condition of no dissociation which occurs at low temperatures is, of course, just the limit of case I where ϵ is zero.

Case II.- At intermediate temperatures the oxygen is completely dissociated and the nitrogen dissociation commences. For this case, ϵ will be defined as the fraction of the initial air which dissociates into nitrogen atoms. Then the compressibility Z is $1.2 + \epsilon$ for this case, and the partial pressures of the components are

$$p(N_2) = x(N_2)p = \frac{0.8-\epsilon}{1.2+\epsilon} \, p \qquad (30a)$$

$$p(N) = x(N)p = \frac{2\epsilon}{1.2+\epsilon} \, p \qquad (30b)$$

$$p(O) = x(O)p = \frac{0.4}{1.2+\epsilon} \, p \qquad (30c)$$

The equilibrium constant for the nitrogen dissociation reaction is

$$K_p(N_2 \rightarrow 2N) = \frac{p^2(N)}{p(N_2)} = \frac{4\epsilon^2 p}{(1.2+\epsilon)(0.8-\epsilon)} \qquad (31)$$

whence ϵ is given by

$$\epsilon = \frac{-0.4 + \sqrt{0.16 + 3.84\left(1+\frac{4p}{K_p}\right)}}{2\left(1+\frac{4p}{K_p}\right)} \qquad (32)$$

Case III.- At high temperatures, the dissociation of nitrogen is also complete, and the ionization of the atoms begins. For this case we assume that the atoms are a single homogeneous species symbolized by N. The term ϵ will now be the fraction of the atoms which have been ionized, and then the partial pressures become

$$p(N) = x(N)p = \frac{1-\epsilon}{1+\epsilon}\,p \tag{33a}$$

$$p(N^+) = x(N^+)p = \frac{\epsilon}{1+\epsilon}\,p \tag{33b}$$

$$p(e^-) = x(e^-)p = \frac{\epsilon}{1+\epsilon}\,p \tag{33c}$$

Note that the compressibility Z in this case is $2(1+\epsilon)$. The ionization reaction equilibrium constant is

$$K_p(N \rightarrow N^+ + e^-) = \frac{p(N^+)p(e^-)}{p(N)} = \frac{\epsilon^2 p}{1-\epsilon^2} \tag{34}$$

and then ϵ becomes

$$\epsilon = \left(1 + \frac{p}{K_p}\right)^{-\frac{1}{2}} \tag{35}$$

The derivatives of the mol fraction compressibility products, Zx_i, will be needed in addition to the mol fractions. For case I, from equations (28), (26a), (26b), and (26c) it is seen that

$$\frac{d \ln K_p}{dT} = \left(\frac{2}{\epsilon} - \frac{1}{1+\epsilon} + \frac{1}{0.2-\epsilon}\right)\left(\frac{\partial \epsilon}{\partial T}\right)_p \tag{36}$$

$$\left[\frac{\partial Zx(O)}{\partial T}\right]_p = 2\left(\frac{\partial \epsilon}{\partial T}\right)_p \tag{37}$$

$$\left[\frac{\partial Zx(O_2)}{\partial T}\right]_p = -\left(\frac{\partial \epsilon}{\partial T}\right)_p \tag{38}$$

$$\left[\frac{\partial Zx(N_2)}{\partial T}\right]_p = 0 \tag{39}$$

where the subscript p refers to the fact that the partial derivatives are taken at constant pressure. In order to find these same partial derivatives at constant density, the equilibrium constant is expressed in concentration units

$$K_c(O_2 \rightarrow 2O) = \frac{4\epsilon^2 n}{(1+\epsilon)(0.2-\epsilon)} = \frac{4\epsilon^2}{0.2-\epsilon} \frac{\rho}{M_O} \qquad (40)$$

whence

$$\frac{d \ln K_c}{dT} = \left(\frac{2}{\epsilon} + \frac{1}{0.2-\epsilon}\right)\left(\frac{\partial \epsilon}{\partial T}\right)_\rho \qquad (41)$$

and the mol fraction derivatives at constant density take the same form as equations (37), (38), and (39) except that the quantity $(\partial \epsilon/\partial T)_p$ is replaced by the quantity $(\partial \epsilon/\partial T)_\rho$ found in equation (41). For case II a similar set of equations for the derivatives occurs

$$\frac{d \ln K_p}{dT} = \left(\frac{2}{\epsilon} - \frac{1}{1.2+\epsilon} + \frac{1}{0.8-\epsilon}\right)\left(\frac{\partial \epsilon}{\partial T}\right)_p \qquad (42a)$$

$$\frac{d \ln K_c}{dT} = \left(\frac{2}{\epsilon} + \frac{1}{0.8-\epsilon}\right)\left(\frac{\partial \epsilon}{\partial T}\right)_\rho \qquad (42b)$$

$$\frac{\partial Zx(N)}{\partial T} = -2\frac{\partial Zx(N_2)}{\partial T} = 2\frac{\partial \epsilon}{\partial T} \qquad (43)$$

$$\frac{\partial Zx(O)}{\partial T} = 0 \qquad (44)$$

Finally, for case III, the equations are

$$\frac{d \ln K_p}{dT} = \left(\frac{2}{\epsilon} - \frac{1}{1+\epsilon} + \frac{1}{1-\epsilon}\right)\left(\frac{\partial \epsilon}{\partial T}\right)_p \qquad (45a)$$

$$\frac{d \ln K_c}{dT} = \left(\frac{2}{\epsilon} + \frac{1}{1-\epsilon}\right)\left(\frac{\partial \epsilon}{\partial T}\right)_\rho \qquad (45b)$$

$$\frac{\partial Zx(N^+)}{\partial T} = \frac{\partial Zx(e^-)}{\partial T} = -\frac{\partial Zx(N)}{\partial T} = 2\frac{\partial \epsilon}{\partial T} \qquad (46)$$

where, as before, the partial derivatives are given for constant pressure or for constant density depending on the corresponding partial derivative of ϵ which is used. With these quantities in hand we are in position to calculate the energy, specific heat, entropy, and the speed of sound for air.

Energy, Specific Heat, Entropy, and Speed of Sound
for Air in Equilibrium

The energy per mol of air is simply the sum

$$E = \sum_i x_i E_i \tag{47}$$

where the E_i are the energy per mol for component i. Generally in
aerodynamic problems the energy per fixed mass of gas is needed rather
than the energy per mol. The mass of gas in a mol of undissociated air
(29 gm) will be used as the constant reference quantity for this purpose.
Then, in dimensionless form, the energy per mol of initially undissociated
air is

$$\frac{ZE}{RT} = Z \sum_i x_i \frac{E_i}{RT} \tag{48}$$

while the dimensionless enthalpy per initial mol of air becomes

$$\frac{ZH}{RT} = \frac{ZE}{RT} + Z \tag{49}$$

The compressibility, Z, and the dimensionless energy, ZE/RT, which
have been calculated from the preceding equations, are listed in
tables IV(a) and IV(b) and are graphed as functions of temperature in
figures 1 and 2. The enthalpy is easily obtained from these values via
equation (49). At this point it is desirable to compare the calculations
of references 9 and 10 with the results obtained above. It is not possi-
ble to compare the numerical results directly since both references 9
and 10 present the properties of air as functions of temperature at con-
stant density rather than at constant pressure as is done here. However,
the results of these two references are the same, and reference 10 tabu-
lates the properties in close enough intervals so that constant pressure
values can be obtained fairly accurately by interpolation. The values
for compressibility and energy interpolated from reference 10 agree with
the approximate solutions within 5 percent in all cases, and generally
within 2 percent, so that on the scale of figures 1 and 2 the differences
are hardly discernible. In view of this agreement, it is concluded that
the solutions presented here are useful approximations for the thermody-
namic properties of air. Therefore we shall proceed to use those approx-
imations to calculate the entropy, specific heats, and speed of sound in
air.

The entropy per initial mol of air is simply obtained from the
entropies of the components of air through the relation

$$\frac{ZS}{R} = Z \left(\sum_i x_i \frac{S_i}{R} - \sum_i x_i \, \ln x_i - \ln \frac{p}{p_0} \right) \tag{50}$$

where p_0 is the reference pressure for the standard state, in this case, 1 atmosphere. The entropy values are listed in table IV(c) and are shown graphically in figure 3.

It is necessary to take the derivatives of the products ZE and ZH for specific heats if the latter are to have their usual meanings, that is, the change in energy which occurs in a fixed mass of gas per degree temperature change. Thus the constant density specific heat per initial mol of air is given by

$$\frac{Z C_v}{R} = \frac{1}{R} \left(\frac{\partial ZE}{\partial T} \right)_\rho = Z \sum_i x_i \frac{C_i}{R} + T \sum_i \left(\frac{E_i}{RT} \right) \left(\frac{\partial Zx_i}{\partial T} \right)_\rho \tag{51}$$

where C_i is the derivative of energy for component i, that is, dE_i/dT. The corresponding specific heat for constant pressure is given by

$$\frac{Z C_p}{R} = \frac{1}{R} \left(\frac{\partial ZH}{\partial T} \right)_p = Z \sum_i x_i \left(\frac{C_i}{R} + 1 \right) + T \sum_i \left(\frac{E_i}{RT} + 1 \right) \left(\frac{\partial Zx_i}{\partial T} \right)_p \tag{52}$$

The specific heats calculated from equations (51) and (52) are listed in tables IV(d) and IV(e). It may be noted that when chemical reactions occur, the difference between the specific heats per mol is not equal to the gas constant, as in an ideal gas, but is given by

$$\left(\frac{C_p}{R} - \frac{C_v}{R} \right) = 1 + \frac{T}{Z} \sum_i \left[\frac{H_i}{RT} \left(\frac{\partial Zx_i}{\partial T} \right)_p - \frac{E_i}{RT} \left(\frac{\partial Zx_i}{\partial T} \right)_\rho \right] \tag{53}$$

Both of the specific heat functions have the same general features. These features are illustrated in figure 4 where the specific heat at constant density is given as a function of temperature for pressures of 0.0001, 0.01, and 1 atmosphere. At low temperature C_v increases from 5/2 R to 7/2 R as the vibrational modes of energy become excited. Then, with increasing temperature, the specific heat goes through three distinct maxima where the chemical components change most rapidly with temperature; the first maximum is due to the oxygen dissociation reaction, the second to the nitrogen dissociation, and the third to the ionization reactions. As pressure decreases, these maxima increase in sharpness and in magnitude and they shift to lower temperatures. It has been pointed out (ref. 16) that the values determined from the partition functions cannot be highly accurate because the second derivatives of the partition

functions are required, and the error in neglecting higher order terms is magnified in the process. However, the curves of figure 4 would merely be shifted slightly in temperature and have somewhat different peak values if the calculations were more exact. Certainly the qualitative features of the specific heats should be correctly given.

The specific heat values determined above enable us to calculate the speed of sound in air. This speed of sound will be defined by

$$a^2 = \left(\frac{\partial p}{\partial \rho}\right)_S \tag{54}$$

that is, the limiting value as the frequency of sound approaches zero. The partial derivative given in equation (54) will not be calculated directly, since it is not convenient to treat the entropy as an independent variable which can be held constant (see eq. (50)). However, equation (54) may be transformed with perfect generality into the form

$$a^2 = \gamma \left(\frac{\partial p}{\partial \rho}\right)_T \tag{55}$$

where γ is the ratio of the specific heats, c_p/c_v. Equation (55) is, in turn, equivalent to

$$a^2 = -\gamma \frac{\left(\frac{\partial p}{\partial T}\right)_\rho}{\left(\frac{\partial \rho}{\partial T}\right)_p} \tag{56}$$

which, from the equation of state (eq. (27)), may be expressed in terms of variables which have already been calculated

$$\frac{a^2 \rho}{p} = \gamma \frac{1 + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_\rho}{1 + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_p} \tag{57}$$

The dimensionless speed of sound parameter, $a^2\rho/p$, is listed in table IV(f) and is plotted as a function of temperature in figure 5. The second term on the right side of equation (57) is generally near unity, so that figure 5 is also indicative of the variation in γ with temperature.

The range of pressure and temperature in which the dissociation of oxygen, the dissociation of nitrogen, and the ionization of atoms are the

important chemical reactions is indicated by dividing table IV into the
regions case I, case II, and case III, respectively. Figure 6 presents
the same information in a graphical form from which it is convenient to
judge the chemical state of air for a given pressure and temperature.
It will be noted that boundaries between the chemical reactions corre-
spond to end points in the characteristic cycles that occur in the
thermodynamic parameters graphed in figures 1 through 5.

Aerodynamic Considerations

The thermodynamic properties obtained at this point are those
required to perform calculations of inviscid air-flow problems by the
method of characteristics. These properties are given for a range of
temperature from $500°$ to $15,000°$ K and of pressure from 0.0001 to
100 atmospheres. It is of interest now to examine the altitude and
velocity at which these conditions will occur in flight. A grid of the
pressure and temperature at the stagnation point of a body in flight is
shown in figure 7 as a function of flight altitude and velocity. The
stagnation enthalpy per unit mass was simply taken as one half the veloc-
ity squared, and the stagnation pressure was related to the static pres-
sure (and thus to altitude) with the results of Feldman (ref. 19), who
computed the pressure ratio developed across normal shock waves in air
at various altitudes. Generally lower temperatures and pressures will
be attained at regions other than the stagnation region, so the range of
these variables will be adequate for such cases also. At very low pres-
sures, such as occur at high altitudes or in expanded flow regions, aero-
dynamic effects may often be disregarded. However, if necessary, the
approximations of this report may be extended to pressures below 0.0001
atmosphere. It is not advisable to extend them to pressures much greater
than 100 atmospheres, since there occurs an increasing overlap of the
chemical reactions in air as pressure increases and, in addition, the
nitric oxide becomes such a large component of the air that it must be
considered. As a result of this overlap in the chemical reactions, the
calculated properties of air show irregularities in the region of transi-
tion from one reaction to another. Slight irregularities can be observed
at the transition regions for 10 and 100 atmosphere pressures (figs. 1
through 4), for example. However, the deviations are small at these pres-
sures and it can be seen from figure 7 that the thermodynamic properties
of air can be closely approximated in closed form over the range of con-
ditions of current interest in aerodynamics. Some of the results of these
approximations will next be used in estimating the transport properties
of high-temperature air.

TRANSPORT PROPERTIES

Collision Cross Sections

Consider first some qualitative aspects of the collisions between gas particles. The particle trajectories are influenced by a potential U which is negligible at long range, which may be attractive or repulsive at intermediate range, but which always becomes strongly repulsive at very short range. A particle with kinetic energy kT will not be greatly deflected if it passes only through that part of the potential field where $|U| \ll kT$. On the other hand, the particle will be deflected appreciably if it passes where $|U| \gg kT$. The direction of the deflection is unimportant so far as transport properties are concerned, for it is the absolute value of the deflection which determines the change in mass, momentum, and energy fluxes caused by the collision. To a first approximation, the absolute value of this deflection is independent of the sign of the potential and the effective collision diameter σ is the order of the largest distance where $U = \pm kT$. The effective collision cross section S will be defined as $\pi\sigma^2$.

In the rigorous treatment of the transport properties of gases, the effective collision cross section S is found to be an integral function of the deflection angles produced by a collision, and this integral is a function of the relative velocity of the colliding particles. The so-called "collision integral" is a function of temperature only which is S times a velocity function integrated over all velocities. Thus the collision integral may be thought of as an average effective collision cross section, and the transport coefficients can be related directly to these integrals. However, not all the interparticle potentials have been developed which are needed to calculate the collision integrals for air. In the present paper then, plausible estimates of the effective collision cross sections will be used to determine the mean free paths for hard elastic spheres, and for such particles the transport coefficients can be related to these mean free paths (ref. 1). The effects of the interaction potentials will be taken into account by letting the spherical cross sections be appropriate functions of temperature.

The effective cross sections for collisions between diatomic molecules can be obtained quite accurately by the collision integral method. However, at high temperatures, the very steep repulsive portion of the intermolecular potential is penetrated so that the molecules do behave essentially like hard spheres. Consistent with the approximations which are to follow, it will be sufficient to use the Sutherland formula for the molecular cross section S_O

$$\frac{S_O}{S_\infty} = 1 + \frac{C}{T} \tag{58}$$

where C is 112° K and S_∞, the molecular cross section at infinite temperature, is $3.14 \times 10^{-15} cm^2$.

For atomic collisions, the picture is complicated by the fact that two atoms may approach each other along any one of a number of potentials.
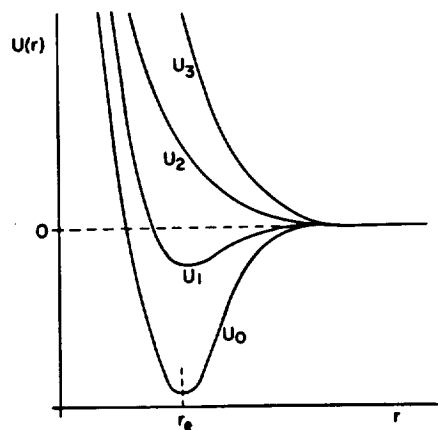
Sketch (a)

For example, the potentials between two normal nitrogen atoms are shown qualitatively in sketch (a) (see ref. 3). The lowest lying of these potentials, designated U_0, has the lowest total electron spin and it is the one normally responsible for the vibrational energy levels observed in the stable molecular state. Therefore U_0 can be expressed quantitatively from experimental spectroscopic data. Unfortunately, the higher lying potentials for the atoms in air are not known quantitatively at present, so we are reduced to estimating an average collision cross section for all of the potentials by means of the known lowest lying potential U_0. For this purpose it is assumed that the collision diameters σ are given by

$$U_0(\sigma) = -kT \tag{59}$$

and these diameters will be used to evaluate the coefficients of momentum and energy transfer. A somewhat deeper penetration of the potential is normally required for a collision to affect the particle flux, so that the diameters σ' which will be used to evaluate the diffusion coefficients are assumed to be given by

$$U_0(\sigma') = -2kT \tag{60}$$

It may be pointed out that Hirschfelder and Eliason (ref. 20) have examined the relation between values of the transport coefficients given by the hard sphere model and by the more rigorous collision integral method. They find that $U(\sigma)$ and $U(\sigma')$ are about $-0.6kT$ for a wide variety of attractive potentials, that $U(\sigma)$ is about $0.9kT$ and $U(\sigma')$ is about $1.6kT$ for a similar variety of repulsive potentials. If all the interparticle potentials were known, it would be simple to use these criteria to obtain a weighted average collision diameter. All the potentials are known for two normal hydrogen atoms (ref. 21) and it is found for this case that equations (59) and (60) yield values for σ and σ' which agree with the weighted average collision diameters within 8 percent over the range of temperatures from $1000°$ to $15,000°$ K. Of course, there is no assurance that these same relations will hold as closely for collisions between the atoms in air. In fact the average collision diameters for normal oxygen and nitrogen atoms will probably be overestimated by equations (59) and (60), since the shallow intermediate potentials (such as U_1 and U_2, sketch (a)) must be considered for these atoms, whereas they do not occur for hydrogen. The effect of these intermediate potentials will be partly compensated for by the fact that some of the atoms will be in excited electronic states which have collision diameters the order of three times larger than the normal atoms (ref. 20). The

fraction of atoms in excited states is small over most of the temperature and pressure range considered so that collisions between excited particles are relatively rare. The encounters between an excited and a normal atom are the ones which significantly influence the mean free paths, and the cross sections for such collisions are about four times normal. The fraction of each constituent in air which is excited is listed as a function of temperature in the following table:

T, $^\circ K$	Fraction of oxygen atoms excited	Fraction of nitrogen atoms excited	Fraction of ionized atoms excited
4,000	0.002	0.002	
6,000	.013	.025	0.012
8,000	.032	.081	.032
10,000	.055	.153	.060
12,000	.079	.228	.089
14,000			.120

The first two excited states of atomic oxygen and of the atomic nitrogen plus ion are very close to the ground state (see table I) and so they have not been counted as excited states. It can be seen that the fraction of excited particles in air will generally be less than 10 percent and in the very worst case considered about 20 percent of the atoms will be excited. This occurs at 100 atmospheres pressure where the ionization reaction is repressed until temperatures beyond 12,000° K are reached and 23 percent of the nitrogen and 8 percent of the oxygen atoms are excited. For a pure gas in which excited particles have three times normal collision diameters, the average mean free path is decreased 28 percent when 10 percent of the particles are excited, and is decreased 45 percent when 20 percent of the particles are excited. Thus the error introduced by neglecting the long-range forces of the excited atoms is probably the same order of magnitude and opposite in effect to the uncertainties caused by neglecting the shortened range of the shallow, intermediate collision potentials.

The lowest lying atom-atom potentials may be approximated by the Morse function

$$U_O = D \left[\left(1 - e^{-\beta\zeta} \right)^2 - 1 \right] \tag{61}$$

where D is the dissociation energy and ζ is the dimensionless distance parameter $(r/r_e - 1)$; r_e is the interatomic distance at which U_O is a minimum (sketch (a)); β is a constant related to the vibrational frequency ν of the stable molecule and is given by $\nu(\pi^2 I/2D)^{1/2}$. Although the Morse function is not very accurate at long ranges, it will be needed only at rather high temperatures where the potential is fairly well described for $|U_O| \geq kT$. The Morse function constants were taken from Herzberg (ref. 3) and these are listed in the following table:

Atomic particles	D/k, $^{\circ}K$	β	r_e, angstroms
O-O	59,000	3.24	1.207
N-N	113,200	2.96	1.094
N-O	75,400	3.18	1.151
O-O$^+$	75,200	3.18	1.123
N-N$^+$	101,200	2.94	1.126

From equations (59) and (61), the momentum and energy transfer collision diameter σ is given by

$$\frac{\sigma}{r_e} = 1 - \beta \ln\left(1 - \sqrt{1 - \frac{kT}{D}}\right) \tag{62a}$$

and by equations (60) and (61) the diffusion collision diameter σ' is given by

$$\frac{\sigma'}{r_e} = 1 - \beta \ln\left(1 - \sqrt{1 - \frac{2kT}{D}}\right) \tag{62b}$$

The atom-molecule collision diameters will be taken as the arithmetic average of the atom-atom and of the molecule-molecule collision diameters. This assumption corresponds to the concept that the collision diameter is a measure of the effective range of the electron distribution about the molecule or atom, and that a collision occurs whenever these electron distributions overlap.

With the onset of ionization, several additional types of collisions must be considered. These are the ion-atom, electron-atom, and the ion-ion, ion-electron, or electron-electron collisions. The ion-atom collisions may be treated in the same manner as the atom-atom collisions, since the spectroscopic data for ionized molecules are available to be used in setting up the Morse potential function between the ion and the neutral atom. The Morse function constants for these cases, which occur in air, are also listed in the preceding table. The ion-ion, ion-electron, and electron-electron collision diameters all depend on long range electrostatic forces of identical magnitude. The criterion for the collision diameter will be taken as before $|U(\sigma)| = kT$. The function U in this case is just the coulomb potential between two charges, and the collision diameter thus becomes

$$\sigma = \frac{e^2}{kT} \tag{63}$$

For electron-atom collisions, the atom will be polarized by the approach of the electron and there will result a charge-dipole type interaction. In order to calculate the magnitude of this interaction, the polarizability of the atom, α, will be needed. The polarizability is defined as the dipole moment produced in the atom by an electric field, E, of unit strength. The interaction energy of the induced dipole moment with the field is $\alpha E^2/2$, and when the field due to the presence of the electron is substituted for E, this energy becomes

$$U = - \frac{e^2 \alpha}{2r^4} \tag{64}$$

It will be noted that the polarizability need not be known with great precision, since the collision diameter depends only on the fourth root of this quantity. Experimental values of polarizability are only given for the molecular state of oxygen and nitrogen. However, Joos (ref. 22) gives an approximate method of calculating the polarizability of atoms in alternating fields which, extrapolated to steady state fields, becomes

$$\alpha = \frac{1}{m} \left(\frac{he}{2\pi I_0} \right)^2 \tag{65}$$

where m in this case is the mass of an electron and I_0 is the resonance potential for ionization of the atom. This resonance potential is 9.11 e.v. for oxygen atoms and 10.28 e.v. for nitrogen atoms (ref. 23). Using these values, one finds the polarizability is 13.2×10^{-25} cm^3 and 10.3×10^{-25} cm^3 for oxygen and nitrogen atoms, respectively.

The collision diameters will enter the calculations to follow in the form of a ratio with the collision diameter for two diatomic molecules at the same temperature. These ratios were calculated by the methods outlined above for those collisions which occur between the major components in high-temperature air. The results are given in table V as functions of temperature. Wherever two or more types of collision give the same result within 5 percent, there is not much point to considering them separately, in view of the other approximations involved. Therefore, for such cases, the values have been weighted and averaged, and only those final averages are given in table V. The atom-molecule cross sections $S(O_2\text{-}O)$, $S(N_2\text{-}N)$, and $S(N_2\text{-}O)$ are very close and these are all designated by the single symbol $S(N_2\text{-}N)$. Similarly the atom-atom and atom-ion cross sections $S(O\text{-}O)$, $S(N\text{-}N)$, $S(N\text{-}O)$, $S(N\text{-}N^+)$, and $S(O\text{-}O^+)$ are all grouped under the notation $S(N\text{-}N)$. The atom-electron cross sections $S(N\text{-}e)$ and $S(O\text{-}e)$ are given the single average value listed under $S(N\text{-}e)$. In the same way, all the atom-molecule and atom-atom diffusion cross sections are given by $S'(N_2\text{-}N)$ and $S'(N\text{-}N)$, respectively. In view of the order of the approximations involved, the electron-atom cross sections for diffusion are not differentiated from the cross sections for momentum and energy transport.

Viscosity

The viscosity of air will be calculated from the simple summation formula for a mixture of hard spherical molecules

$$\eta = \frac{5\pi}{32} \sum_i \rho_i u_i \lambda_i \tag{66}$$

In view of the other approximations involved, a more sophisticated formulation than this does not seem warranted. The constant $5\pi/32$ is chosen to agree with the value which accounts for the persistence in velocity of the higher speed molecules (ref. 1). It will be convenient to use, as a reference value, the viscosity which air would have at the same temperature if the molecules did not dissociate or ionize

$$\eta_o = \frac{5\pi}{32} \rho_o u_o \lambda_o \tag{67}$$

In cgs units, this reference viscosity becomes

$$\eta_o = 1.462 \times 10^{-5} \frac{\sqrt{T}}{1+112/T} \frac{gm}{cm\text{-}sec} \tag{68}$$

where T is the absolute temperature in degrees Kelvin. The ratio of mean velocities is

$$\frac{u_i}{u_o} = \sqrt{\frac{M_o}{M_i}} \tag{69}$$

and the ratio of densities, where the total number of moles per unit volume is the same, is

$$\frac{\rho_i}{\rho_o} = \frac{M_i}{M_o} x_i \tag{70}$$

Under these same conditions, that is, the same mol concentration, the ratio of mean free paths is (ref. 1)

$$\frac{\lambda_o}{\lambda_i} = \sum_j x_j \frac{S_{ij}}{S_o} \left(\frac{1 + \frac{M_i}{M_j}}{2} \right)^{1/2} \tag{71}$$

Then the ratio of viscosity to the reference viscosity becomes

$$\frac{\eta}{\eta_0} = \sum_i \sqrt{\frac{M_i}{M_0}} \; x_i \; \frac{\lambda_i}{\lambda_0} \tag{72}$$

Before equation (71) can be applied to the case where ionization occurs, it must be observed that the atom-electron collisions are not to be counted in evaluating the atom mean free paths, nor are the ion-electron collisions to be counted in evaluating the ion mean free paths. This is because the mean free path which occurs in the derivation of viscosity is the mean distance between those collisions which cause a relatively large change in momentum of the particle being considered, either in direction or in magnitude. Normally all collisions qualify in this sense, but when a heavy particle like an atom or an ion collides with an extremely light particle like an electron, there is practically no change in the momentum of the heavy particle, and this momentum is carried intact to the first collision with another heavy particle.

A feature of the ionized gas which should be mentioned is that charged particles under the influence of coulomb potentials may be deflected by the cumulative effect of many long-range collisions. Then, as pointed out by Cohen, Spitzer, and Routly (ref. 24), the effective collision cross section is larger than for a single collision at short range. However, a charge-shielding effect limits the range of the coulomb potential and where charge density is large the correction to the collision cross section is small. For the range of variables treated here, collisions with neutral particles generally predominate when the charge density is small. Thus, in the first approximation, the mean free path is considered to be a consequence of single, independent collisions as in equation (71).

The coefficients of viscosity for high-temperature air have been calculated from equations (68), (71), and (72) and the results are presented in table VI(a) and in figure 8. The terms in the summation of equation (72) will also be used in the evaluation of the coefficient of thermal conductivity which follows.

Thermal Conductivity

A theory for the thermal conductivity of a chemically reacting gas was perhaps first outlined by Nernst (ref. 25). The form in which this theory has been developed by Hirschfelder (ref. 15) will be used here to calculate the conductivity of high-temperature air. In this theory the energy transfer through the gas is treated in two independent parts. The first part is the energy transferred by molecular collisions, and this mode of energy transfer is the one responsible for the ordinary thermal conductivity of nonreacting gases. The second part is the energy transferred by diffusion of the molecular species and the reactions which occur as the gas tends to maintain itself in chemical equilibrium at each

point. We shall first turn attention to the calculation of energy transferred by molecular collisions. If one invokes Eucken's assumption (ref. 26), that the internal energy is distributed among the gas particles independently of their velocity distribution, then the simple linearized expression for the coefficient of thermal conductivity in a mixed gas becomes

$$k_n = \frac{5\pi}{32} \sum_i \rho_i u_i \frac{\lambda_i}{M_i} \left(\frac{5}{2} C_t + C_{int} \right)_i \qquad (73)$$

where C_t is the specific heat per mol due to translational energy and C_{int} the specific heat due to the internal energy. It is noted that

$$C_i = (C_t + C_{int})_i \qquad (74)$$

and

$$C_t = \frac{3}{2} R \qquad (75)$$

whence equation (73) becomes

$$k_n = \frac{5\pi}{32} \sum_i \rho_i u_i \lambda_i \left(\frac{C_i}{M_i} + \frac{9}{4} \frac{R}{M_i} \right) \qquad (76)$$

It will be convenient to define a reference coefficient of thermal conductivity just as was done for the viscosity, that is, the value air would have if it did not vibrate, dissociate, or ionize. This coefficient will be

$$k_o = \frac{19}{4} \frac{R}{M_o} \eta_o \qquad (77)$$

or in cgs units

$$k_o = 1.364 \, \eta_o \, \frac{\text{joule}}{\text{cm-sec } ^\circ K} \qquad (78)$$

where η_o is in gm/cm-sec.

The ratio of the thermal conductivity coefficient to the reference coefficient becomes

$$\frac{k_n}{k_0} = \sum_i \left(\sqrt{\frac{M_i}{M_0}} \; x_i \; \frac{\lambda_i}{\lambda_0} \right) \frac{M_0}{M_i} \left[\frac{4}{19} \left(\frac{c}{R} \right)_i + \frac{9}{19} \right] \tag{79}$$

The first factors in each term are just the terms already calculated for the viscosity. It may be noted that the same collisions are to be neglected in this case as for viscosity. This is because these electron-atom and electron-ion collisions have only a small effect on the magnitude and direction for the energy flux vector of the heavy particles. Actually, all of the electron collisions could have been neglected for the purpose of computing viscosity, for the electrons carry a negligible fraction of the total momentum transferred, due to their small mass. However, because of its high velocity, an electron transports a large share of the kinetic energy, in fact much more than a heavier gas particle. Therefore the heat conduction terms for the electrons are needed in equation (79).

The second mode of energy transfer, which takes place whenever the gas undergoes a chemical reaction, is due to the diffusion of the chemical species. These particles then react with one another, giving off or absorbing the heat of reaction and causing heat transfer which may be considerably larger than the ordinary heat transfer due to molecular collisions. Hirschfelder (ref. 15) has formulated this problem, but in terms of the multicomponent diffusion coefficients which are difficult to estimate. However, Butler and Brokaw (ref. 27) have shown how Hirschfelder's results can be modified to make use of the binary diffusion coefficients instead, and their solutions are in convenient form for computational purposes. Moreover, Butler and Brokaw show that Hirschfelder's method of predicting thermal conductivity agrees very well with the experimental results for a number of gases which dissociate or react chemically at ordinary temperatures. Therefore we shall be able to apply this method with some confidence. That part of the coefficient of thermal conductivity which is due to the chemical reaction will be designated k_r, and according to the results of reference 27, this may be expressed as

$$k_r = \frac{R \left(T \, \dfrac{d \ln K_p}{dT} \right)^2}{\displaystyle\sum_i \sum_j \frac{a_i}{n D_{ij} x_i} (a_i x_j - a_j x_i)} \tag{80}$$

where D_{ij} is the binary diffusion coefficient for molecules of type i into molecules of type j, and the a_i are the stoichiometric coefficients of components A_i in the chemical reaction written in the form

$$\sum_i a_i A_i = 0 \tag{81}$$

According to reference 1, the binary diffusion coefficients are given by

$$\frac{1}{nD_{ij}} = \frac{8}{3} \sqrt{\frac{2}{\pi}} \left(\frac{M_i M_j}{M_i + M_j}\right)^{1/2} \frac{N_o}{(RT)^{1/2}} S'_{ij} \tag{82}$$

Now the reference coefficient of thermal conductivity (eq. (77)) can be put in the form

$$k_o = \frac{95\sqrt{\pi}}{64} \frac{R}{N_o S_o} \sqrt{\frac{RT}{M_o}} \tag{83}$$

Substituting equation (82) in equation (80) and dividing by equation (83), one obtains

$$\frac{k_r}{k_o} = \frac{\dfrac{12\sqrt{2}}{95} \left(T \dfrac{d \ln K_p}{dT}\right)^2}{\displaystyle\sum_i \sum_j \left[\frac{M_i M_j}{M_o(M_i + M_j)}\right]^{1/2} \frac{S'_{ij}}{S_o} \frac{a_i}{x_i} (a_i x_j - a_j x_i)} \tag{84}$$

In order to simplify the computations somewhat, the differences in mass between oxygen and nitrogen atoms will be neglected. Then, since some of the collision cross sections may also be given the same value, the double summations in the denominator of equation (84) take on the relatively simple form as follows:

For case I (oxygen dissociation reaction only)

$$\sum_i \sum_j = \frac{S'(N_2-N)}{\sqrt{3}\,S_o} \left\{ \frac{[x(O)+2x(O_2)]^2}{x(O)x(O_2)} + \frac{4x(N_2)}{x(O)} \right\} + \frac{x(N_2)}{\sqrt{2}\,x(O_2)} \tag{85}$$

for case II (nitrogen dissociation reaction only)

$$\sum_i \sum_j = \frac{S'(N_2-N)}{\sqrt{3}\ S_o} \left\{ \frac{[x(N)+2x(N_2)]^2}{x(N)x(N_2)} + \frac{x(0)}{x(N_2)} \right\} + \frac{S'(N-N)}{S_o} \frac{2x(0)}{x(N)} \tag{86}$$

and finally for case III (ionization reaction only)

$$\sum_i \sum_j = \left[\frac{1}{2} \frac{S'(N-N)}{S_o} + \frac{1}{230} \frac{S'(N-e^-)}{S} \right] \frac{[x(N)+x(N^+)]^2}{x(N)x(N^+)} \tag{87}$$

The total coefficient of thermal conductivity is just the sum, k_n+k_r. The values of this sum were calculated for air and the results are presented in table VI(b) and graphed in figure 9. The coefficient of thermal conductivity has about the same functional features with respect to temperature and pressure that were observed for the specific heat (fig. 4). The Prandtl numbers were calculated from the relation

$$Pr = \frac{c_p \eta}{\overline{M}k} = \frac{4}{19} \left(\frac{Zc_p}{R} \right) \frac{\eta/\eta_o}{k/k_o} \tag{88}$$

and they are listed in table VI(c) and are graphed as functions of temperature in figure 10.

As noted, nitrogen and oxygen have approximately equal collision cross sections, so that up to the point where ionization begins, air can be treated essentially as a two-component mixture of atoms and molecules. Then it is possible to characterize the system with a single diffusion coefficient, and the differential equations of fluid flow may be analyzed while keeping the terms describing heat transfer by chemical reaction separate from the terms describing ordinary thermal conduction. This method is followed, for example, by Fay and Riddell (ref. 28) in their analysis for the heat transfer to the stagnation region of blunt bodies in high-speed flight. In using such an analysis, it must be realized that the thermodynamic and transport coefficients are defined somewhat differently than in the present paper. The coefficients which appear in reference 28 will be called the "partial coefficients" and they will be designated here by a superscript prime. The partial specific heat, the partial coefficient of thermal conductivity, the partial Prandtl number, and the partial Lewis number, respectively, are related to the quantities defined in this paper as follows:

$$\left.\begin{aligned}
C_p{}' &= \sum x_i(C_i + 1) \\[2ex]
k' &= k_n \\[2ex]
Pr' &= \frac{C_p{}'\eta}{\overline{M}k'} \\[2ex]
Le' &= \frac{D\rho C_p{}'}{\overline{M}k'}
\end{aligned}\right\} \qquad (89)$$

The partial Lewis number, Le', appears as a coefficient for the chemical reaction terms in reference 28. The diffusion coefficient D is the ordinary binary diffusion coefficient D_{ij} given by equation (82), and from equation (83) a dimensionless group is

$$\frac{ZD\rho R}{k_0 M_0} = 0.309 \left[\frac{S'(N_2-N)}{S_0}\right]^{-1} \qquad (90)$$

The Lewis number is conveniently calculated from the expression

$$Le' = \frac{ZD\rho R}{k_0 M_0} \frac{ZC_p{}'/R}{Zk_n/k_0} \qquad (91)$$

Table VII lists the calculated values for the partial coefficients $ZC_p{}'/R$, k_n/k_0, Pr', and Le'. The numbers Pr' and Le' are also graphed as functions of temperature in figure 11. The partial coefficients are not given for temperatures where ionization occurs because the air is then at least a three-component system (neutral atoms, ionized atoms, and electrons) and the partial coefficients, as defined, do not apply to this case. It can be seen that Pr' is a relatively constant quantity with an average value about 0.72. The partial Lewis number, on the other hand, decreases as dissociation proceeds to completion. From the result that the partial Prandtl number is approximately constant, it follows that the factor $C_p{}'/\overline{M}k'$ decreases as η^{-1}. The factor $D\rho/\overline{M}$ increases at about the same rate (see eq. (82) or (90)), and the product of these two factors is relatively constant; thus the partial Lewis number varies approximately as $\overline{M}$, that is, it decreases by a factor of about 2, from about 1.4 to 0.6.

A list of conversion factors is given in table VIII for convenience in converting the tabulated and graphed parameters into dimensioned units.

DISCUSSION OF RESULTS

It is convenient to summarize the physical processes which influence the transport properties of air in a discussion of the variations in Prandtl number with temperature. At low temperatures the air is like a pure diatomic gas with a specific heat about $7/2$ R. From equation (88), the Prandtl number for such a gas is $14/19$ or 0.74. As temperature increases, vibrational energy is excited in the molecules so that C_p approaches $9/2$ R, while from equation (76) the thermal conductivity approaches $(23/4)(R\eta_o/M_o)$. For this limit the Prandtl number becomes $18/23$ or 0.78.

At still higher temperatures the oxygen dissociates and both C_p and k go through the pronounced maxima shown in figures 4 and 9. To a first approximation, k is about proportional to C_p just as for a nonreacting gas. However, due to the influence of the chemical reaction, the maximum in k occurs at slightly lower temperatures than the maximum in specific heat as indicated in sketch (b). The viscosity coefficient is not greatly influenced by the oxygen dissociation, so from equation (88) it is apparent that the Prandtl number will follow an S shaped function as shown in sketch (b). This shape for the function can be seen in the curves of figure 10.
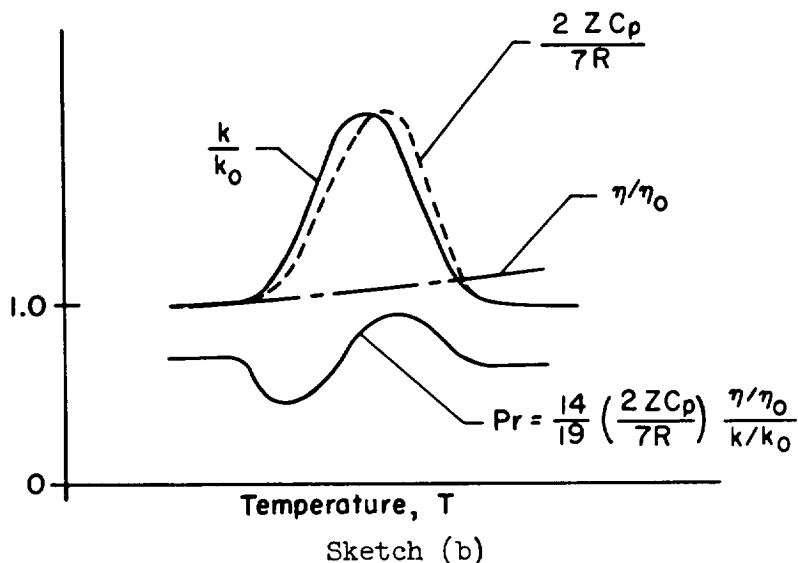
Sketch (b)

At the temperature where oxygen dissociation is essentially complete and nitrogen dissociation has not yet begun, the Prandtl number can be calculated for a two-component mixture from the known conditions that the mol fractions are $x_1 = 2/3$ and $x_2 = 1/3$ and that the molecular weights are related by $M_1 = 2M_2$ (where subscript 1 refers to nitrogen molecules and subscript 2 to oxygen atoms). If the collision cross sections are all assumed equal, the mean free paths are related by

$$\frac{\lambda_2}{\lambda_1} = \frac{4+\sqrt{6}}{2+\sqrt{3}} \tag{92}$$

Then the Prandtl number becomes

$$\left(\frac{C_p}{M}\right)\left(\frac{\eta}{k}\right) = \left(\frac{23}{5}\frac{R}{M_1}\right)\left[\frac{1 + \frac{\sqrt{2}}{4}\frac{\lambda_2}{\lambda_1}}{\frac{R}{M_1}\left(\frac{23}{4} + \frac{15\sqrt{2}}{8}\frac{\lambda_2}{\lambda_1}\right)}\right] \approx 0.72 \tag{93}$$

which checks closely with the values for Prandtl number shown in figure 10 at the transitions from oxygen to nitrogen dissociation.

As nitrogen dissociation proceeds, the Prandtl number again follows an S shaped function of temperature for the same reasons which were outlined for oxygen dissociation (sketch (b)). The fully dissociated air is like a pure monatomic gas with C_p about 5/2 R and k equal 15/4 $(R\eta/M)$, so that the Prandtl number approaches 2/3. The Prandtl numbers of figure 10 go through this value of 2/3 at a temperature where the dissociation is essentially complete but the ionization is still negligible (Z = 2, fig. 1).

Up to this point, the Prandtl numbers lie within the range from 0.6 to 1.0 in agreement with the conclusions of reference 29. However, when ionization begins, the Prandtl number may drop to somewhat lower values. For very small degrees of ionization it can be shown that the ratio of electron to atom mean free path is about $\sqrt{2}$ and that the coefficient of viscosity is influenced very little by the presence of the electrons. However, the thermal conductivity is greatly increased by the electrons because of their high thermal velocity, and the effect is illustrated in figure 9 by the abrupt change in slope for k where the ionization reaction first begins. If the fraction of ionization, ϵ, is so small that chemical reaction terms may be neglected

$$k = \frac{15}{4}\frac{R}{M_1}\eta\left(1 + \epsilon\sqrt{\frac{2M_1}{M_2}}\right) \tag{94}$$

where M_1 is the atom mass and M_2 the electron mass. It can be seen that k increases rapidly with the onset of ionization because the factor $(2M_1/M_2)^{1/2}$ is large, about 230. Accordingly the Prandtl number is found to vary as

$$\left(\frac{C_p}{M}\right)\left(\frac{\eta}{k}\right) = \left(\frac{5}{2}\frac{R}{M_1}\right)\left[\frac{15}{4}\frac{R}{M_1}\left(1 + \epsilon\sqrt{\frac{2M_1}{M_2}}\right)\right]^{-1} = \frac{2}{3(1+230\epsilon)} \tag{95}$$

A very small value of ϵ is sufficient to reduce the Prandtl number considerably below 2/3, the value for a pure monatomic gas. As the ionization proceeds, however, the chemical reaction terms which were omitted in equations (94) and (95) become predominant such that C_p becomes approximately proportional to k again, and the Prandtl number levels out at about 0.3 as shown in figure 10. At this point another factor gradually predominates, namely the decrease in coefficient of viscosity which occurs as the mean free paths become very short as a result of the long range coulomb forces acting on the charged gas particles. Consider, for example, the completely ionized gas. The mol fraction of ions (subscript 1) equals the mol fraction of electrons (subscript 2) and the collision cross sections are about equal. Then the ratio of mean free paths is

$$\frac{\lambda_2}{\lambda_1} = \frac{\sqrt{2}}{1+\sqrt{2}} \qquad (96)$$

where, as before, the electron collisions do not count toward the ion mean free paths. The ratio k/η is approximately given by

$$\frac{k}{\eta} \simeq \frac{15}{4} \frac{R}{M_1} \frac{\sqrt{2}}{1+\sqrt{2}} \sqrt{\frac{M_1}{M_2}} \qquad (97)$$

and with $C_p/\overline{M}$ about $5R/M_1$, the Prandtl number becomes very small

$$\frac{C_p}{\overline{M}} \frac{\eta}{k} \simeq \frac{4}{3} \frac{1+\sqrt{2}}{\sqrt{2}} \sqrt{\frac{M_2}{M_1}} = 0.014 \qquad (98)$$

as shown in figure 10. With the assumption that the Prandtl number retains its usual significance, boundary-layer regions in highly ionized flow should be much better heat conductors than in the flow of neutral gas particles. This result is of theoretical interest even though fully ionized air flow will not be obtained at flight velocities below escape speed (figs. 6 and 7).

The Prandtl number functions of figure 10 are similar to those predicted by Kaeppeler and Krause (ref. 30). Their calculations were based on the low value for nitrogen dissociation energy and so the present estimates exhibit more distinctly separate maxima. This is because of the separation between the dissociation reactions which occurs when the higher value for nitrogen dissociation energy is used. Greifinger (ref. 31) has also made some estimates for the transport properties of air at high temperatures. He assumes constant collision cross sections in a manner such that, up to the point where ionization begins, his calculated Prandtl number is a constant lacking the structure shown in figure 10. However, reference 31 predicts the same order of effect due to ionization which has been discussed here.

Recall that the nitric oxide in air has been neglected and that the calculated thermodynamic properties of air are not greatly affected by this omission. It is not obvious that the transport properties of air will be similarly independent of NO formation, since NO is ionized rather easily compared to N_2 and O_2 molecules. Practically all of the electrons which appear in air at intermediate temperatures come from the NO ionization reaction. However, Gilmore finds that the quantity of such electrons is very small, the order of 0.01 percent or less (ref. 9), and from equations (94) and (95) it can be judged that this amount is not yet sufficient to alter greatly the transport properties of air.

At present there are no direct measurements of the transport properties for air at the high temperatures considered here. One experimental comparison which can be made at the moment is to insert the calculated coefficients into a theory for the heat transfer to a simple aerodynamic shape, and then compare the results with measured heat-transfer rates. For example, reference 32 compares the values for heat flux to the stagnation region of a blunt body in high-energy air flow which were measured by Rose and Riddell (ref. 33) with the theoretical predictions based on the transport coefficients developed in the present report. It is found that the calculated heat flux deviates less than 10 percent from the mean of the measured data. This is a favorable result in view of the approximations involved in the theory and of the scatter in the experimental data (the order of ±20 percent). It should be emphasized that this comparison is not a sufficient test for the reliability of the calculated transport coefficients, as it is possible that errors in the coefficients compensate for each other or for approximations in the heat-transfer analysis. Nevertheless, the favorable comparison is reassuring inasmuch as it means that at least a necessary condition for the correctness of the theories is fulfilled.

CONCLUDING REMARKS

In conclusion, the thermodynamic properties (including compressibility, energy, entropy, specific heat, and the speed of sound) and the transport properties (the coefficients of viscosity and thermal conductivity and the Prandtl number) have been estimated for air at high temperatures. These estimates were made from approximations in closed form, and it is found that these approximations give fairly accurately the thermodynamic properties over the range of pressures and temperatures for flight through the atmosphere. The transport properties were calculated by methods which have given reasonably good results for gases at ordinary temperatures and for gases which dissociate and react chemically. Moreover, the values calculated for the transport properties can be used to predict the same order of heating rates that have been measured at the stagnation region of blunt bodies in high-energy air flow. Therefore it is concluded that the results presented in this paper are useful engineering approximations for the properties of high-temperature air. In particular, it is an advantage that the solutions appear in closed form because the functional

relationships can be visualized. In addition the air properties can conveniently be computed in very small intervals to give tables that can be used in obtaining solutions to real air flow by the method of characteristics, or for numerical solutions of boundary-layer flow. It is expected that the calculated coefficients of viscosity and thermal conductivity will prove to be lower bounds to more precise calculations or measurements. The prediction that the Prandtl number for highly ionized flow will be small compared to unity is of interest, for it implies that boundary-layer regions in such a gas will be very transparent to heat flux.

Ames Aeronautical Laboratory
        National Advisory Committee for Aeronautics
            Moffett Field, Calif., Nov. 18, 1957

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TABLE I.- PARTITION FUNCTION CONSTANTS FOR THE MAJOR COMPONENTS OF AIR

Particle	Molecular weight, M, gm/mol	Rotational constant, $\dfrac{ah^2}{8\pi^2 Ik}$, °K	Vibrational constant, $\dfrac{hv}{k}$, °K	Dissociation energy, $\dfrac{D}{k}$, °K	Electronic degeneracy, g_n	Electronic energy, $\dfrac{\epsilon_n}{k}$, °K	Ionization energy, $\dfrac{I}{k}$, °K
N_2	28	5.78	3390	113,200	1	0	
O_2	32	4.16	2270	59,000	3	0	
					2	11,390	
					2	18,990	
O	16				5	0	158,000
					3	228	
					1	326	
					5	22,800	
					1	48,600	
N	14				4	0	168,800
					10	27,700	
					6	41,500	
O^+	16				4	0	
					10	38,600	
					6	58,200	
N^+	14				1	0	
					3	70.6	
					5	188.9	
					5	22,000	
					1	47,000	
					5	67,900	
e^-	$\dfrac{1}{1820}$				2	0	

TABLE II.- THERMODYNAMIC PROPERTIES FOR THE MAJOR COMPONENTS OF AIR

T, °K	(a) Logarithm of the partition function for a standard state of one atmosphere, $\ln Q_p$ — Particle							(b) Dimensionless energy, $\dfrac{E-E_0}{RT}$ — Particle							(c) Dimensionless specific heat, $\dfrac{1}{R}\dfrac{dE}{dT}$ — Particle						
	N_2	O_2	N	O	N^+	O^+	e^-	N_2	O_2	N	O	N^+	O^+	e^-	N_2	O_2	N	O	N^+	O^+	e^-
500	21.33	22.97						2.51	2.55						2.55	2.72					
1,000	23.79	25.49		19.86				2.62	2.76		1.60				2.92	3.16					
1,500	25.28	27.05		20.90				2.76	2.93		1.57				3.16	3.37		1.52			
2,000	26.39	28.20	20.68	21.64				2.88	3.05	1.50	1.55				3.29	3.46	1.50	1.51			
2,500	27.26	29.12	21.24	22.21				2.97	3.15	1.50	1.54				3.36	3.62	1.51	1.50			
3,000	27.99	29.88	21.70	22.67				3.04	3.23	1.50	1.54				3.40	3.71	1.52	1.51			
3,500	28.62	30.54	22.08	23.06				3.09	3.31	1.51	1.54				3.42	3.80	1.56	1.52			
4,000	29.17	31.12	22.42	23.40				3.14	3.38	1.52	1.54				3.44	3.88	1.62	1.54			
4,500	29.66	31.64	22.72	23.70				3.17	3.44	1.53	1.54				3.45	3.94	1.71	1.56			
5,000	30.10	32.10	22.98	23.97	23.77	23.18	7.06	3.20	3.49	1.56	1.55	1.56	1.51	1.50	3.46	3.97	1.82	1.59	1.63	1.57	1.50
5,500	30.50	32.54	23.23	24.21	24.01	23.41	7.30	3.22	3.53	1.59	1.56	1.56	1.52		3.47	4.00	1.94	1.62	1.66	1.61	
6,000	30.87	32.93	23.46	24.43	24.23	23.63	7.52	3.24	3.57	1.62	1.57	1.57	1.53		3.47	4.00	2.07	1.65	1.69	1.67	
6,500	31.21	33.30	23.67	24.64	24.44	23.84	7.72	3.26	3.60	1.66	1.58	1.58	1.54		3.48	3.99	2.19	1.68	1.72	1.74	
7,000	31.52	33.64	23.86	24.83	24.63	24.02	7.90	3.28	3.63	1.70	1.59	1.59	1.56		3.48	3.98	2.30	1.70	1.74	1.82	
7,500	31.82		24.05	25.01	24.81	24.20	8.07	3.29	3.65	1.75	1.60	1.60	1.58		3.48	3.96	2.40	1.72	1.75	1.91	
8,000	32.10		24.23	25.18	24.98	24.37	8.24	3.30	3.67	1.79	1.60	1.61	1.60		3.48	3.96	2.49	1.74	1.77	2.00	
8,500	32.36		24.40	25.34	25.14	24.53	8.39	3.31	3.69	1.83	1.61	1.62	1.63		3.49	3.94	2.55	1.76	1.78	2.09	
9,000	32.60		24.57	25.49	25.29	24.68	8.53	3.32	3.70	1.87	1.62	1.63	1.66		3.49	3.92	2.61	1.77	1.79	2.18	
9,500	32.84		24.72	25.63	25.43	24.82	8.66	3.33	3.71	1.91	1.63	1.64	1.69		3.49	3.90	2.64	1.77	1.80	2.26	
10,000	33.06		24.87	25.76	25.57	24.96	8.79	3.34	3.72	1.95	1.64	1.65	1.72		3.49	3.88	2.66	1.78	1.81	2.34	
10,500			25.02	25.89	25.70	25.10	8.92			1.98	1.64	1.66	1.75				2.67	1.78	1.82	2.41	
11,000			25.16	26.01	25.82	25.22	9.03			2.02	1.65	1.66	1.78				2.67	1.78	1.82	2.46	
11,500			25.29	26.13	25.94	25.35	9.14			2.04	1.66	1.67	1.81				2.65	1.78	1.83	2.52	
12,000			25.42	26.25	26.05	25.47	9.25			2.07	1.66	1.68	1.84				2.64	1.78	1.83	2.56	
12,500			25.55	26.35	26.16	25.58	9.35			2.09	1.67	1.68	1.87				2.61	1.78	1.84	2.60	
13,000			25.67	26.46	26.27	25.70	9.45			2.11	1.67	1.69	1.90				2.57	1.78	1.84	2.63	
13,500			25.78	26.56	26.37	25.81	9.54			2.13	1.68	1.70	1.93				2.55	1.77	1.84	2.65	
14,000			25.90	26.68	26.46	25.91	9.63			2.14	1.68	1.70	1.95				2.52	1.77	1.84	2.66	
14,500			26.01	26.75	26.56	26.02	9.72			2.15	1.68	1.71	1.98				2.48	1.76	1.85	2.66	
15,000			26.12	26.84	26.65	26.12	9.81			2.16	1.68		2.00				2.45	1.76	1.85	2.66	

Note: In columns (b) e^- and (c) e^- the value 1.50 is shown with a horizontal arrow, indicating it remains constant at 1.50 for all temperatures $\geq$ 5,000 °K.

TABLE III.- LOGARITHMS OF THE CHEMICAL EQUILIBRIUM CONSTANTS AND THEIR DERIVATIVES
FOR THE MAJOR REACTIONS IN AIR

T, °K	(a) $\ln K_p$ Reaction				(b) $T \dfrac{d \ln K_p}{dT}$ Reaction			
	$O_2 \rightarrow 2O$	$N_2 \rightarrow 2N$	$O \rightarrow O^{+}+e^{-}$	$N \rightarrow N^{+}+e^{-}$	$O_2 \rightarrow 2O$	$N_2 \rightarrow 2N$	$O \rightarrow O^{+}+e^{-}$	$N \rightarrow N^{+}+e^{-}$
500	-44.78				60.43			
1,000	-24.58				40.54			
1,500	-14.42	-41.62			30.56	57.72		
2,000	-8.30	-30.06			24.53	46.31		
2,500	-4.20	-22.33			20.51	38.70		
3,000	-1.27	-16.80			17.62	33.27		
3,500	.94	-12.63			15.45	29.20		
4,000	2.65	-9.38			13.76	26.05		
4,500	4.03	-6.77			12.41	23.55		
5,000	5.16	-4.62	-25.33	-25.92	11.31	21.53	34.06	36.26
5,500	6.10	-2.82	-22.25	-22.61	10.40	19.87	31.19	33.17
6,000	6.90	-1.29	-19.62	-19.84	9.63	18.47	28.79	30.59
6,500	7.59	.03	-17.40	-17.48	8.97	17.31	26.77	28.39
7,000	8.19	1.19	-15.48	-15.45	8.40	16.30	25.04	26.51
7,500	8.72	2.22	-13.80	-13.68	7.91	15.43	23.55	24.86
8,000	9.18	3.13	-12.32	-12.12	7.48	14.67	22.25	23.42
8,500	9.60	3.95	-11.01	-10.74	7.10	14.00	21.10	22.15
9,000	9.98	4.69	-9.83	-9.50	6.76	13.41	20.09	21.01
9,500	10.32	5.37	-8.77	-8.39	6.46	12.88	19.19	20.00
10,000			-7.81	-7.39			18.38	19.08
10,500			-6.93	-6.48			17.65	18.25
11,000			-6.12	-5.65			16.99	17.49
11,500			-5.38	-4.89			16.39	16.81
12,000			-4.70	-4.19			15.84	16.18
12,500			-4.06	-3.54			15.34	15.60
13,000			-3.47	-2.94			14.88	15.07
13,500			-2.91	-2.38			14.46	14.57
14,000			-2.40	-1.86			14.06	14.12
14,500			-1.91	-1.37			13.69	13.69
15,000			-1.45	-.91			13.35	13.30

TABLE IV.- THERMODYNAMIC PROPERTIES FOR AIR

(a) Compressibility, Z

T, °K	Case							
		100	10	1.0	0.1	0.01	0.001	0.0001
500	Case I Oxygen dissociation	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1,000		1.000	1.000	1.000	1.000	1.000	1.000	1.000
1,500		1.000	1.000	1.000	1.000	1.000	1.000	1.000
2,000		1.000	1.000	1.000	1.001	1.002	1.005	1.016
2,500		1.000	1.001	1.003	1.011	1.033	1.087	1.163
3,000		1.003	1.009	1.026	1.072	1.149	1.192	1.201
3,500		1.012	1.035	1.091	1.152	1.196	1.204	1.211
4,000		1.033	1.088	1.164	1.195	1.209	1.228	1.287
4,500		1.070	1.147	1.191	1.214	1.244	1.336	1.575
5,000		1.115	1.180	1.217	1.252	1.358	1.620	1.908
5,500		1.153	1.215	1.248	1.347	1.597	1.896	1.987
6,000		1.176	1.237	1.316	1.527	1.847	1.987	2.010
6,500	Case II Nitrogen dissociation	1.226	1.280	1.436	1.750	1.958	2.010	2.032
7,000		1.250	1.351	1.605	1.900	1.988	2.028	2.088
7,500		1.287	1.456	1.775	1.940	2.022	2.068	2.210
8,000		1.343	1.589	1.891	1.986	2.046	2.144	2.446
8,500		1.417	1.722	1.950	2.028	2.090	2.284	2.827
9,000		1.510	1.832	1.990	2.052	2.166	2.510	3.282
9,500		1.612	1.904	2.020	2.092	2.286	2.834	3.646
10,000		1.713	1.970	2.048	2.150	2.462	3.202	3.844
10,500		1.799	2.024	2.074	2.236	2.700	3.528	3.932
11,000		1.864	2.036	2.112	2.352	2.984	3.746	3.969
11,500		1.910	2.052	2.176	2.506	3.274	3.868	3.986
12,000		1.941	2.074	2.234	2.696	3.522	3.930	3.993
12,500	Case III Ionization	1.996	2.102	2.320	2.912	3.700	3.962	3.996
13,000		2.021	2.138	2.426	3.136	3.818	3.980	3.998
13,500		2.058	2.182	2.554	3.348	3.890	3.988	3.999
14,000		2.074	2.234	2.700	3.526	3.932	3.994	3.999
14,500		2.102	2.320	2.912	3.700	3.962	3.996	4.000
15,000		2.120	2.374	3.030	3.770	3.998	3.998	4.000

(b) Dimensionless energy, $\dfrac{ZE}{RT}$

Pressure, atmospheres

T, °K	100	10	1.0	0.1	0.01	0.001	0.0001
500	2.52	2.52	2.52	2.52	2.52	2.52	2.52
1,000	2.65	2.65	2.65	2.65	2.65	2.65	2.65
1,500	2.80	2.80	2.80	2.80	2.80	2.80	2.80
2,000	2.92	2.92	2.92	2.93	2.96	3.06	3.40
2,500	3.02	3.03	3.09	3.27	3.78	5.05	6.84
3,000	3.13	3.25	3.58	4.48	5.98	6.82	7.00
3,500	3.33	3.71	4.65	5.65	6.39	6.57	6.81
4,000	3.66	4.46	5.56	6.00	6.33	6.86	8.52
4,500	4.12	5.10	5.66	6.13	6.88	9.19	15.17
5,000	4.58	5.32	5.91	6.71	9.10	15.00	21.5
5,500	4.86	5.66	6.33	8.37	13.51	19.63	20.7
6,000	4.96	5.89	7.37	11.36	17.39	19.90	19.9
6,500	5.51	6.45	9.18	14.66	18.30	19.31	20.2
7,000	5.76	7.40	11.30	16.36	17.79	18.67	22.0
7,500	6.18	8.75	13.63	16.16	17.59	19.49	26.2
8,000	6.82	10.37	14.73	16.11	17.32	21.6	32.9
8,500	7.65	11.83	14.94	16.21	17.50	25.2	40.4
9,000	8.67	12.86	14.95	16.08	18.36	30.2	45.5
9,500	9.67	13.30	15.02	16.22	19.89	35.6	47.1
10,000	10.60	13.60	14.86	16.71	22.3	39.8	46.7
10,500	11.29	13.75	14.86	17.61	25.3	41.8	45.5
11,000	11.70	13.78	15.04	18.97	29.0	42.2	44.0
11,500	11.89	13.66	15.50	20.8	32.9	41.7	42.6
12,000	11.95	13.68	16.05	23.0	35.5	40.8	41.2
12,500	12.16	13.85	16.86	25.5	36.9	39.7	39.9
13,000	12.30	14.12	17.90	27.9	37.4	38.6	38.7
13,500	12.44	14.48	19.16	29.9	37.3	37.5	37.6
14,000	12.49	15.24	20.6	31.4	36.7	36.5	36.6
14,500	12.48	15.56	22.7	32.8	36.1	36.1	35.6
15,000	12.44		23.6		35.6	35.6	

(c) Dimensionless entropy, $\dfrac{ZS}{R}$

Pressure, atmospheres

T, °K	100	10	1.0	0.1	0.01	0.001	0.0001
500	21.1	23.9	25.7	28.0	30.3	32.6	34.9
1,000	23.7	26.0	28.3	30.6	32.9	35.2	37.5
1,500	25.3	27.6	29.9	32.2	34.5	36.8	39.2
2,000	26.6	28.9	31.2	33.5	35.8	38.2	40.9
2,500	27.5	29.9	32.2	34.7	37.6	41.4	45.8
3,000	28.4	30.8	33.5	36.9	41.0	44.6	47.6
3,500	29.3	32.0	35.4	39.1	42.6	45.6	48.6
4,000	30.2	33.5	37.3	40.5	43.6	46.9	51.5
4,500	31.3	34.9	38.2	41.5	45.1	50.4	59.4
5,000	32.3	35.8	39.2	42.9	48.4	58.0	68.8
5,500	33.3	36.8	40.8	45.5	54.2	64.7	71.2
6,000	33.9	37.7	42.2	49.6	59.9	66.9	72.2
6,500	35.0	38.9	44.9	54.3	62.5	68.1	73.4
7,000	35.8	40.5	48.3	57.4	63.9	69.1	75.3
7,500	36.8	42.7	51.6	58.6	64.7	70.5	78.7
8,000	38.0	45.1	53.8	59.8	65.7	72.5	84.6
8,500	39.4	47.4	55.1	61.0	67.0	76.1	93.2
9,000	41.0	49.4	56.0	63.0	69.0	81.1	103.0
9,500	42.7	50.7	57.0	64.5	71.7	87.8	110.6
10,000	44.4	51.9	57.8	66.4	75.3	95.0	114.8
10,500	46.4	53.1	58.6	68.6	79.9	100.9	116.8
11,000	47.5	53.6	59.6	71.4	85.0	105.4	118.0
11,500	47.7	54.2	61.1	74.7	90.1	109.2	118.8
12,000	48.3	54.8	62.1	78.3	94.4	110.1	119.3
12,500	49.2	55.5	63.7	81.8	97.4	110.8	119.8
13,000	49.9	56.3	65.5	85.1	99.5	111.3	120.2
13,500	50.6	57.2	67.6	87.8	100.9	111.8	120.7
14,000	51.2	58.1	69.8	90.1	101.8	112.2	121.1
14,500	51.7	59.5	72.8	91.6	102.6	112.6	121.5
15,000	52.2	60.4	74.6		103.4		121.9

Case I — Oxygen dissociation
Case II — Nitrogen dissociation
Case III — Ionization

TABLE IV.- THERMODYNAMIC PROPERTIES FOR AIR – Concluded

(d) Dimensionless specific heat at constant density, $\frac{1}{R}\left(\frac{\partial ZE}{\partial T}\right)_\rho$

Case	T, °K	Pressure, atmospheres
		100	10	1.0	0.1	0.01	0.001	0.0001
Case I — Oxygen dissociation	500	2.59	2.59	2.59	2.59	2.59	2.59	2.59
	1,000	2.96	2.96	2.96	2.96	2.96	2.96	2.96
	1,500	3.20	3.20	3.20	3.20	3.20	3.20	3.20
	2,000	3.33	3.33	3.33	3.54	3.98	5.49	10.12
	2,500	3.55	3.69	4.37	6.40	11.60	20.7	17.45
	3,000	3.94	5.05	7.99	14.10	14.97	6.25	3.75
	3,500	5.05	7.82	12.32	11.55	4.61	5.23	8.99
	4,000	6.64	10.06	8.64	4.33	6.96	14.16	35.9
	4,500	8.00	8.45	4.66	7.74	16.87	42.2	85.1
	5,000	7.94	5.46	7.56	16.20	39.3	72.3	40.6
	5,500	6.57	6.61	13.27	31.4	59.7	37.5	9.39
	6,000	5.11	9.91	22.5	46.9	40.8	10.60	8.27
Case II — Nitrogen dissociation	6,500	7.36	15.03	33.5	44.0	15.96	7.86	16.02
	7,000	9.96	21.6	39.5	24.7	7.44	13.36	31.7
	7,500	13.17	28.0	33.8	16.57	10.45	23.0	60.1
	8,000	17.11	31.5	21.8	7.46	15.92	38.8	100.6
	8,500	21.0	29.5	13.08	11.05	24.1	62.5	139.4
	9,000	23.9	23.1	6.52	15.06	36.3	90.7	139.0
	9,500	25.0	16.34	8.52	20.9	52.1	114.5	94.1
	10,000	23.4	8.77	12.49	28.3	70.0	116.2	49.0
	10,500	20.3	8.54	15.79	37.5	86.5	92.0	25.1
	11,000	16.33	9.76	19.82	48.1	95.1	59.6	15.14
	11,500	12.80	11.40	24.8	59.1	90.3	35.4	10.81
	12,000	10.15	13.37	30.3	68.4	53.4	21.9	8.76
	12,500	5.27	15.47	36.1	73.6	36.8	14.20	7.82
Case III — Ionization	13,000	6.82	18.06	42.3	73.5	24.8	10.82	7.39
	13,500	10.05	20.9	47.9	66.8	17.73	9.16	7.01
	14,000	11.14	24.0	53.1	56.8	11.95	8.38	7.02
	14,500	12.81	28.6	57.5	42.3	7.63	7.66	7.02
	15,000	13.55	30.5	56.8	34.4		7.33	7.03

(e) Dimensionless specific heat at constant pressure, $\frac{1}{R}\left(\frac{\partial ZH}{\partial T}\right)_p$

Case	T, °K	Pressure, atmospheres
		100	10	1.0	0.1	0.01	0.001	0.0001
Case I — Oxygen dissociation	500	3.59	3.59	3.59	3.59	3.59	3.59	3.59
	1,000	3.96	3.96	3.96	3.96	3.96	3.96	3.96
	1,500	4.20	4.20	4.20	4.20	4.20	4.20	4.20
	2,000	4.33	4.33	4.33	4.56	5.03	6.65	11.66
	2,500	4.56	4.71	5.37	7.68	13.47	23.9	20.2
	3,000	5.01	6.24	9.55	16.60	17.68	7.77	4.98
	3,500	6.27	9.45	14.79	13.94	5.97	6.55	10.58
	4,000	8.18	12.32	10.68	9.34	8.44	16.30	40.7
	4,500	9.93	10.60	6.06	18.90	19.46	48.7	101.2
	5,000	10.04	7.04	9.18	37.1	46.0	87.0	47.4
	5,500	8.46	8.16	15.69	57.2	72.4	44.4	11.97
	6,000	6.68	11.96	26.8	54.0	49.2	13.37	10.59
Case II — Nitrogen dissociation	6,500	9.08	18.04	49.2	30.2	13.37	16.18	19.07
	7,000	12.17	26.2	42.1	20.5	9.84	27.0	36.6
	7,500	16.09	34.8	27.2	9.88	19.57	45.4	69.8
	8,000	21.2	40.0	16.52	13.73	28.5	74.4	121.2
	8,500	26.4	37.5	8.79	18.29	43.0	111.0	173.3
	9,000	30.6	29.4	10.96	34.0	62.8	144.1	172.8
	9,500	32.2	20.7	15.49	45.6	86.3	146.7	114.6
	10,000	30.6	11.51	19.40	59.3	109.5	114.8	59.4
	10,500	26.2	11.02	24.2	74.0	115.1	73.3	31.2
	11,000	21.2	12.44	37.4	87.5	93.1	43.8	20.2
	11,500	16.71	14.35	45.1	95.8	67.2	28.2	15.30
	12,000	13.36	16.74	53.9	96.3	46.6	19.26	13.00
	12,500	7.34	19.35	62.2	87.5	32.0	15.40	11.93
Case III — Ionization	13,000	9.15	22.7	69.5	73.5	23.6	13.50	11.44
	13,500	13.03	26.3	76.0	54.4	17.42	12.59	11.00
	14,000	14.33	30.3	76.1	44.6	11.73	11.76	11.02
	14,500	16.41	36.5				11.38	11.02
	15,000	17.50	39.5					11.03

(f) Dimensionless speed of sound parameter, $a^2\frac{\rho}{p}$

Case	T, °K	Pressure, atmospheres
		100	10	1.0	0.1	0.01	0.001	0.0001
Case I — Oxygen dissociation	500	1.39	1.39	1.39	1.39	1.39	1.39	1.39
	1,000	1.34	1.34	1.34	1.34	1.34	1.34	1.34
	1,500	1.31	1.31	1.31	1.31	1.31	1.31	1.31
	2,000	1.30	1.30	1.30	1.29	1.25	1.21	1.14
	2,500	1.29	1.28	1.23	1.19	1.14	1.12	1.13
	3,000	1.27	1.23	1.18	1.15	1.15	1.24	1.33
	3,500	1.23	1.19	1.17	1.17	1.29	1.25	1.17
	4,000	1.21	1.19	1.21	1.30	1.21	1.14	1.10
	4,500	1.21	1.22	1.29	1.20	1.11	1.10	1.09
	5,000	1.22	1.27	1.21	1.14	1.13	1.13	1.12
	5,500	1.24	1.23	1.16	1.16	1.11	1.24	1.27
	6,000	1.29	1.19	1.14	1.14	1.14	1.29	1.28
Case II — Nitrogen dissociation	6,500	1.22	1.17	1.14	1.14	1.20	1.20	1.18
	7,000	1.20	1.15	1.14	1.14	1.24	1.15	1.13
	7,500	1.18	1.16	1.16	1.17	1.19	1.13	1.12
	8,000	1.18	1.17	1.19	1.20	1.16	1.12	1.11
	8,500	1.18	1.22	1.23	1.32	1.14	1.12	1.11
	9,000	1.18	1.29	1.34	1.23	1.13	1.13	1.12
	9,500	1.20	1.28	1.19	1.18	1.13	1.14	1.13
	10,000	1.21	1.26	1.18	1.16	1.14	1.17	1.17
	10,500	1.23	1.24	1.16	1.16	1.15	1.20	1.24
	11,000	1.25	1.23	1.15	1.15	1.16	1.26	1.32
	11,500	1.28	1.22	1.17	1.15	1.18	1.34	1.41
	12,000	1.37	1.21	1.16	1.16	1.21	1.42	1.48
	12,500	1.34	1.21	1.17	1.16	1.26	1.47	1.52
Case III — Ionization	13,000	1.28	1.21	1.17	1.17	1.31	1.50	1.55
	13,500	1.26	1.20	1.18	1.18	1.43	1.53	1.57
	14,000	1.26	1.20	1.18	1.19	1.54	1.55	1.57
	14,500	1.25	1.20	1.18	1.21			1.57
	15,000	1.26	1.20	1.19	1.24			1.57

TABLE V.- COLLISION CROSS SECTIONS

T, °K	S_O, in 10^{-16} cm2	$\dfrac{S(N_2-N)}{S_O}$	$\dfrac{S(N-N)}{S_O}$	$\dfrac{S(N-e)}{S_O}$	$\dfrac{S(e-e)}{S_O}$	$\dfrac{S'(N_2-N)}{S_O}$	$\dfrac{S'(N-N)}{S_O}$
500	38.4	0.946	0.894			0.877	0.761
1,000	34.9	.920	.838			.843	.703
1,500	33.7	.889	.785			.817	.652
2,000	33.2	.886	.742			.794	.611
2,500	32.8	.846	.705			.775	.578
3,000	32.6	.830	.676			.759	.551
3,500	32.4	.815	.650			.745	.527
4,000	32.3	.803	.628			.733	.507
4,500	32.2	.792	.608			.722	.489
5,000	32.1	.782	.591			.712	.473
5,500	32.0	.773	.575	0.397	89.9	.703	.458
6,000	32.0	.764	.561	.380	75.6	.695	.445
6,500	31.9	.757	.548	.366	64.5	.688	.433
7,000	31.9	.750	.536	.353	55.7	.681	.422
7,500	31.9	.743	.524	.342	48.6	.674	.412
8,000	31.8	.737	.514	.331	42.8	.668	.402
8,500	31.8	.731	.504	.321	37.9	.662	.393
9,000	31.8	.725	.495	.313	33.8	.657	.385
9,500	31.8	.720	.486	.304	30.4	.652	.377
10,000	31.8	.715	.478	.297	27.4	.647	.370
10,500	31.7	.710	.470	.290	24.9	.642	.363
11,000	31.7	.706	.463	.283	22.7	.637	.356
11,500	31.7	.701	.456	.281	20.8	.633	.350
12,000	31.7	.697	.448	.270	19.09	.629	.342
12,500	31.7	.693	.443	.266	17.60	.625	.338
13,000	31.7	.689	.437	.261	16.27	.621	.332
13,500	31.7		.431	.256	15.10		.327
14,000	31.7		.426	.252	14.04		.322
14,500	31.6		.420	.247	13.09		.316
15,000	31.6		.415	.243	12.24		.312

$S(N_2-N) = S(O_2-O) = S(N_2-O)$
$S(N-N) = S(O-O) = S(N-O) = S(N-N^+) = S(O-O^+)$
$S(N-e^-) = S(O-e^-)$
$S'(N_2-N) = S'(O_2-O) = S'(N_2-O)$
$S'(N-N) = S'(O-O) = S'(N-O) = S'(N-N^+) = S'(O-O^+)$

TABLE VI.- TRANSPORT PROPERTIES OF AIR

T, $^\circ K$	Ratio η/η_0							Reference coefficient, η_0, in 10^{-6}	
	Pressure, atmospheres							$\dfrac{\text{lb sec}}{\text{ft}^2}$	$\dfrac{\text{gm}}{\text{cm-sec}}$
	100	10	1.0	0.1	0.01	0.001	0.0001		
500	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.558	267
1,000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	.868	416
1,500	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.100	527
2,000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.293	619
2,500	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.461	700
3,000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.612	772
3,500	1.000	1.001	1.003	1.006	1.010	1.010	1.011	1.751	838
4,000	1.003	1.008	1.016	1.020	1.022	1.024	1.032	1.879	899
4,500	1.010	1.022	1.029	1.033	1.038	1.055	1.096	1.999	957
5,000	1.022	1.036	1.043	1.051	1.074	1.128	1.181	2.11	1011
5,500	1.036	1.052	1.060	1.086	1.146	1.209	1.227	2.22	1062
6,000	1.050	1.067	1.090	1.148	1.228	1.257	1.259	2.32	1112
6,500	1.072	1.090	1.139	1.229	1.276	1.289	1.277	2.42	1159
7,000	1.089	1.124	1.208	1.294	1.317	1.309	1.273	2.52	1204
7,500	1.112	1.175	1.283	1.332	1.342	1.315	1.221	2.61	1247
8,000	1.143	1.238	1.342	1.371	1.355	1.291	1.086	2.69	1289
8,500	1.185	1.307	1.386	1.392	1.354	1.220	.841	2.78	1330
9,000	1.238	1.368	1.425	1.405	1.328	1.085	.534	2.86	1370
9,500	1.298	1.418	1.447	1.404	1.267	.871	.280	2.94	1408
10,000	1.361	1.468	1.460	1.389	1.162	.615	.1397	3.02	1446
10,500	1.418	1.497	1.467	1.352	1.004	.384	.0788	3.10	1482
11,000	1.467	1.515	1.464	1.287	.806	.226	.0556	3.17	1518
11,500	1.509	1.529	1.450	1.190	.597	.1362	.0466	3.24	1552
12,000	1.549	1.543	1.425	1.065	.415	.0930	.0435	3.31	1586
12,500	1.577	1.542	1.376	.908	.279	.0688	.0436	3.38	1620
13,000	1.592	1.539	1.312	.741	.1918	.0598	.0453	3.45	1652
13,500	1.617	1.528	1.230	.580	.1363	.0569	.0471	3.52	1684
14,000	1.628	1.508	1.129	.443	.1061	.0572	.0506	3.58	1716
14,500	1.631	1.460	.968	.306	.0843	.0576	.0543	3.65	1747
15,000	1.640	1.436	.882	.254	.0615	.0598	.0581	3.71	1777

TABLE VI.- TRANSPORT PROPERTIES OF AIR - Continued

	(b) Coefficient of thermal conductivity								
T, $^\circ K$	Ratio k/k_O							Reference coefficient, k_O, in 10^{-6}	
	Pressure, atmospheres							Btu	watt
	100	10	1.0	0.1	0.01	0.001	0.0001	ft sec $^\circ R$	cm $^\circ K$
500	1.021	1.021	1.021	1.021	1.021	1.021	1.021	5.84	364
1,000	1.100	1.100	1.100	1.100	1.100	1.100	1.100	9.10	567
1,500	1.150	1.150	1.150	1.150	1.150	1.150	1.150	11.53	719
2,000	1.177	1.177	1.177	1.251	1.460	2.09	3.99	13.55	844
2,500	1.256	1.317	1.619	2.50	4.63	7.67	5.50	15.31	954
3,000	1.421	1.928	3.20	5.48	5.02	2.19	1.465	16.90	1053
3,500	1.941	3.15	4.72	3.96	1.719	2.11	3.71	18.35	1143
4,000	2.69	3.94	2.99	1.600	2.91	6.04	15.03	19.69	1227
4,500	3.22	3.06	1.714	3.32	7.34	17.65	30.5	21.0	1305
5,000	3.07	1.997	3.29	7.18	16.63	25.8	11.84	22.1	1379
5,500	2.46	2.91	5.99	13.71	22.2	11.40	3.54	23.3	1449
6,000	1.930	4.53	10.19	18.74	13.09	3.96	7.30	24.3	1516
6,500	3.35	6.98	14.50	15.39	5.49	7.18	14.69	25.4	1580
7,000	4.69	9.97	15.69	8.32	3.28	12.82	29.0	26.4	1642
7,500	6.31	12.48	12.24	5.92	10.47	22.3	54.3	27.3	1701
8,000	8.21	13.19	7.80	3.42	16.37	37.5	87.6	28.2	1759
8,500	9.86	11.55	5.10	11.99	25.0	59.3	110.9	29.1	1814
9,000	10.90	8.79	3.26	16.83	37.5	82.4	97.5	30.0	1868
9,500	10.88	6.38	10.09	23.6	52.8	96.5	59.1	30.8	1921
10,000	9.87	4.07	15.44	32.0	69.0	90.3	30.2	31.6	1972
10,500	8.33	11.18	19.84	41.8	81.2	64.9	16.54	32.4	2020
11,000	6.84	13.44	25.1	52.9	83.7	40.0	11.41	33.2	2070
11,500	5.59	16.25	31.2	63.2	74.2	24.9	9.54	34.0	2120
12,000	4.79	19.56	38.2	70.9	57.6	17.18	8.98	34.7	2160
12,500	3.34	23.0	45.0	73.2	41.4	13.07	9.08	35.5	2210
13,000	11.11	27.0	52.2	69.8	29.6	11.67	9.50	36.2	2250
13,500	17.62	31.3	58.2	61.5	22.0	11.37	9.98	36.9	2300
14,000	20.0	35.7	62.6	51.1	17.92	11.61	10.73	37.6	2340
14,500	23.3	42.1	65.3	38.7	15.24	11.93	11.51	38.2	2380
15,000	25.3	45.3	64.2	33.1	12.72	12.52	12.31	38.9	2420

TABLE VI.- TRANSPORT PROPERTIES OF AIR - Concluded

(c) Prandtl number						
$T,$ $°K$	Pressure, atmospheres					
	100	10	1.0	0.1	0.01	0.001	0.0001
500	0.738	0.738	0.738	0.738	0.738	0.738	0.738
1,000	.756	.756	.756	.756	.756	.756	.756
1,500	.767	.767	.767	.767	.767	.767	.767
2,000	.773	.773	.773	.766	.724	.668	.614
2,500	.762	.751	.696	.645	.611	.654	.771
3,000	.740	.680	.627	.636	.740	.745	.714
3,500	.678	.631	.660	.744	.737	.658	.606
4,000	.640	.662	.762	.759	.619	.580	.587
4,500	.654	.743	.752	.610	.578	.611	.764
5,000	.702	.767	.611	.581	.624	.799	.993
5,500	.748	.620	.583	.617	.785	.989	.871
6,000	.763	.592	.602	.736	.969	.891	.384
6,500	.610	.592	.673	.906	.955	.383	.348
7,000	.593	.620	.796	.986	.830	.346	.337
7,500	.595	.688	.927	.969	.350	.334	.330
8,000	.620	.788	.983	.648	.332	.328	.316
8,500	.666	.891	.943	.335	.324	.321	.276
9,000	.730	.961	.807	.321	.320	.307	.1987
9,500	.806	.966	.330	.314	.316	.273	.1140
10,000	.886	.872	.308	.310	.313	.210	.0577
10,500	.937	.310	.301	.309	.284	.1427	.0312
11,000	.955	.294	.296	.303	.246	.0870	.0207
11,500	.947	.284	.295	.293	.1945	.0503	.0157
12,000	.908	.277	.293	.276	.1409	.0321	.0132
12,500	.728	.272	.290	.250	.0949	.0213	.0120
13,000	.275	.272	.284	.215	.0634	.0166	.0115
13,500	.251	.270	.276	.1733	.0416	.0142	.0109
14,000	.245	.269	.263	.1338	.0293	.0130	.0109
14,500	.241	.265	.237	.0903	.0202	.0119	.0109
15,000	.238	.263	.220	.0719	.0119	.0114	.0109

TABLE VII.- PARTIAL COEFFICIENTS

(a) Specific heat, $\dfrac{zC_p'}{R} = z \sum x_i \left(\dfrac{c_i}{R} + 1\right)$

T, °K	Pressure, atmospheres						
	100	10	1.0	0.1	0.01	0.001	0.0001
500	3.59	3.59	3.59	3.59	3.59	3.59	3.59
1,000	3.96	3.96	3.96	3.96	3.96	3.96	3.96
1,500	4.20	4.20	4.20	4.20	4.20	4.20	4.20
2,000	4.33	4.33	4.33	4.33	4.33	4.33	4.34
2,500	4.41	4.41	4.41	4.41	4.42	4.45	4.47
3,000	4.46	4.47	4.47	4.48	4.51	4.52	4.53
3,500	4.50	4.52	4.52	4.54	4.56	4.55	4.56
4,000	4.53	4.55	4.57	4.58	4.58	4.60	4.65
4,500	4.57	4.59	4.60	4.61	4.64	4.74	4.97
5,000	4.60	4.66	4.64	4.68	4.81	5.12	5.46
5,500	4.62	4.71	4.71	4.85	5.20	5.62	5.76
6,000	4.64	4.82	4.85	5.20	5.73	5.94	6.00
6,500	4.72	5.00	5.12	5.71	6.11	6.21	6.25
7,000	4.78	5.28	5.53	6.16	6.35	6.44	6.56
7,500	4.89	5.68	6.02	6.40	6.58	6.68	6.97
8,000	5.04	6.06	6.42	6.66	6.78	6.97	7.57
8,500	5.27	6.42	6.66	6.91	6.97	7.34	8.41
9,000	5.55	6.66	6.87	6.98	7.20	7.85	9.35
9,500	5.85	6.89	6.98	7.11	7.49	8.54	10.11
10,000	6.15	7.02	7.07	7.26	7.86	9.29	10.52
10,500	6.41	7.05	7.12	7.45	8.34	9.95	10.73
11,000	6.59	7.06	7.20	7.67	8.91	10.41	10.84
11,500	6.71	7.07	7.33	7.97	9.49	10.67	10.91
12,000	6.76	7.10	7.39	8.33	9.99	10.82	10.94
12,500	6.88	7.11	7.54	8.75	10.37	10.90	10.98
13,000	6.86	7.17	7.71	9.20	10.62	10.96	10.99
13,500	6.91	7.23	7.95	9.63	10.77	10.99	11.01
14,000	6.90	7.37	8.24	10.01	10.87	11.00	11.02
14,500	6.90	7.44	8.66	10.37	10.94	11.01	11.02
15,000	6.88		8.88	10.52	11.02	11.02	11.03

(b) Thermal conductivity ratio, $\dfrac{k_n}{k_0}$

T, °K	Pressure, atmospheres						
	100	10	1.0	0.1	0.01	0.001	0.0001
500	1.021	1.021	1.021	1.021	1.021	1.021	1.021
1,000	1.100	1.100	1.100	1.100	1.100	1.100	1.100
1,500	1.150	1.150	1.150	1.150	1.150	1.150	1.150
2,000	1.177	1.177	1.177	1.177	1.177	1.178	1.181
2,500	1.195	1.195	1.196	1.198	1.206	1.225	1.252
3,000	1.205	1.208	1.215	1.235	1.268	1.285	1.289
3,500	1.218	1.230	1.259	1.289	1.310	1.314	1.320
4,000	1.238	1.270	1.312	1.329	1.340	1.356	1.406
4,500	1.269	1.319	1.346	1.366	1.396	1.482	1.674
5,000	1.311	1.357	1.389	1.428	1.541	1.777	1.983
5,500	1.351	1.406	1.448	1.569	1.829	2.08	2.14
6,000	1.383	1.457	1.566	1.824	2.14	2.25	3.66
6,500	1.459	1.543	1.767	2.14	2.33	3.95	4.37
7,000	1.519	1.685	2.05	2.38	2.47	4.73	4.93
7,500	1.606	1.889	2.33	2.52	4.99	5.35	5.34
8,000	1.733	2.14	2.55	2.66	5.71	5.87	5.57
8,500	1.898	2.40	2.70	5.91	6.33	6.26	5.58
9,000	2.10	2.61	2.83	6.65	6.87	6.52	5.46
9,500	2.32	2.78	6.39	7.34	7.33	6.63	5.47
10,000	2.53	2.93	7.52	7.95	7.69	6.66	5.72
10,500	2.71	7.32	8.28	8.50	7.96	6.76	6.15
11,000	2.86	8.16	9.00	9.01	8.16	7.02	6.69
11,500	2.97	9.01	9.67	9.45	8.36	7.41	7.28
12,000	3.06	9.88	10.34	9.86	8.63	8.00	7.91
12,500	3.17	10.66	10.95	10.23	9.03	8.62	8.57
13,000	8.70	11.46	11.55	10.59	9.54	9.29	9.26
13,500	11.18	12.25	12.13	11.00	10.15	10.00	9.98
14,000	12.11	13.02	12.69	11.47	10.83	10.74	10.73
14,500	13.13	13.79	13.18	11.98	11.56	11.51	11.51
15,000	13.97	14.55	13.81	12.68	12.32	12.32	12.31

TABLE VII.- PARTIAL COEFFICIENTS - Concluded

(c) Prandtl number, Pr'

T, °K	Pressure, atmospheres						
	100	10	1.0	0.1	0.01	0.001	0.0001
2,000	0.775	0.775	0.774	0.773	0.772	0.772	0.772
2,500	.777	.777	.773	.773	.770	.763	.750
3,000	.776	.772	.756	.762	.747	.739	.738
3,500	.771	.758	.743	.744	.738	.734	.734
4,000	.764	.747	.739	.738	.726	.729	.717
4,500	.753	.739	.732	.732	.725	.708	.683
5,000	.744	.732	.724	.723	.704	.682	.683
5,500	.740	.724	.709	.705	.684	.686	.694
6,000	.728	.715	.693	.687	.691	.697	
6,500	.720	.700	.684	.689	.703		
7,000	.711	.690	.696	.703	.711		
7,500	.698	.690	.710	.710			
8,000	.691	.693	.719	.721			
8,500	.687	.707	.734				
9,000	.687	.714					
9,500	.695	.725					
10,000	.704						
10,500	.710						
11,000	.716						
11,500	.719						
12,000	.719						
12,500							

(d) Lewis number, Le'

T, °K	Pressure, atmospheres						
	100	10	1.0	0.1	0.01	0.001	0.0001
2,000	1.408	1.407	1.404	1.355	1.355	1.346	1.335
2,500	1.445	1.437	1.405	1.391	1.355	1.233	1.172
3,000	1.464	1.424	1.320	1.327	1.213	1.157	1.147
3,500	1.449	1.347	1.225	1.227	1.167	1.154	1.143
4,000	1.404	1.265	1.196	1.180	1.144	1.130	1.051
4,500	1.327	1.215	1.158	1.160	1.114	.998	.786
5,000	1.268	1.167	1.115	1.105	.970	.750	.609
5,500	1.235	1.131	1.019	.982	.762	.610	.580
6,000	1.158	1.071	.885	.808	.628	.578	
6,500	1.118	.975	.746	.669	.588		
7,000	1.059	.860	.652	.605	.574		
7,500	.979	.756	.601	.587			
8,000	.893	.669	.570	.570			
8,500	.805	.618	.567				
9,000	.726	.584					
9,500	.662	.558					
10,000	.618						
10,500	.585						
11,000	.564						
11,500	.531						
12,000	.525						
12,500							

TABLE VIII.- CONVERSION FACTORS

Multiply	By	To get	In
$\dfrac{ZE}{RT}$ or $\dfrac{ZH}{RT}$	0.0686 T (°K) 0.287 T (°K) 0.0686 T (°R) 1716 T (°R)	Energy or enthalpy	cal/gm joule/gm Btu/lb mass ft-lb/slug
$\dfrac{ZS}{R}$, $\dfrac{ZC_v}{R}$, $\dfrac{ZC_p}{R}$, or $\dfrac{ZC_p'}{R}$	0.0686 0.287 0.0686 1716	Entropy or specific heat	cal/gm °K joule/gm °K Btu/lb mass °R ft-lb/slug °R
η/η_0	$1.462\times10^{-5}\,T^{1/2}\left(1 + \dfrac{112}{T}\right)^{-1}$ (T in °K) $2.28\times10^{-8}\,T^{1/2}\left(1 + \dfrac{202}{T}\right)^{-1}$ (T in °R)	Coefficient of viscosity	$\dfrac{\text{gm}}{\text{cm-sec}}$ lb sec/ft²
$\dfrac{k}{k_0}$ or $\dfrac{k_n}{k_0}$	$4.76\times10^{-6}\,T^{1/2}\left(1 + \dfrac{112}{T}\right)^{-1}$ (T in °K) $1.994\times10^{-5}\,T^{1/2}\left(1 + \dfrac{112}{T}\right)^{-1}$ (T in °K) $2.40\times10^{-6}\,T^{1/2}\left(1 + \dfrac{202}{T}\right)^{-1}$ (T in °R) $1.867\times10^{-3}\,T^{1/2}\left(1 + \dfrac{202}{T}\right)^{-1}$ (T in °R)	Coefficient of thermal conductivity	$\dfrac{\text{cal}}{\text{cm-sec °K}}$ $\dfrac{\text{watt}}{\text{cm °K}}$ $\dfrac{\text{Btu}}{\text{ft-sec °R}}$ $\dfrac{\text{ft-lb}}{\text{ft-sec °R}}$
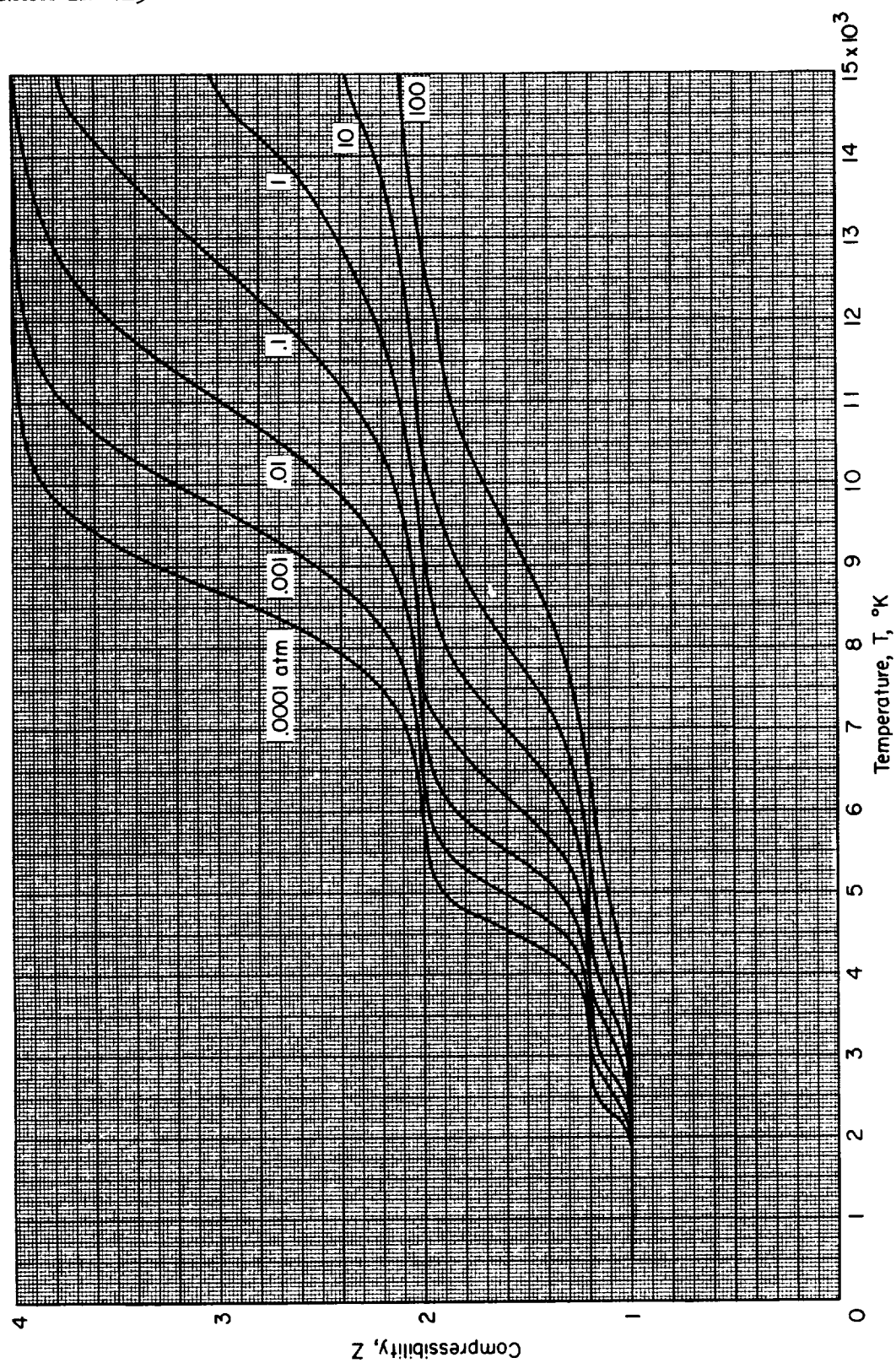
Figure 1.- Compressibility of air as a function of temperature.
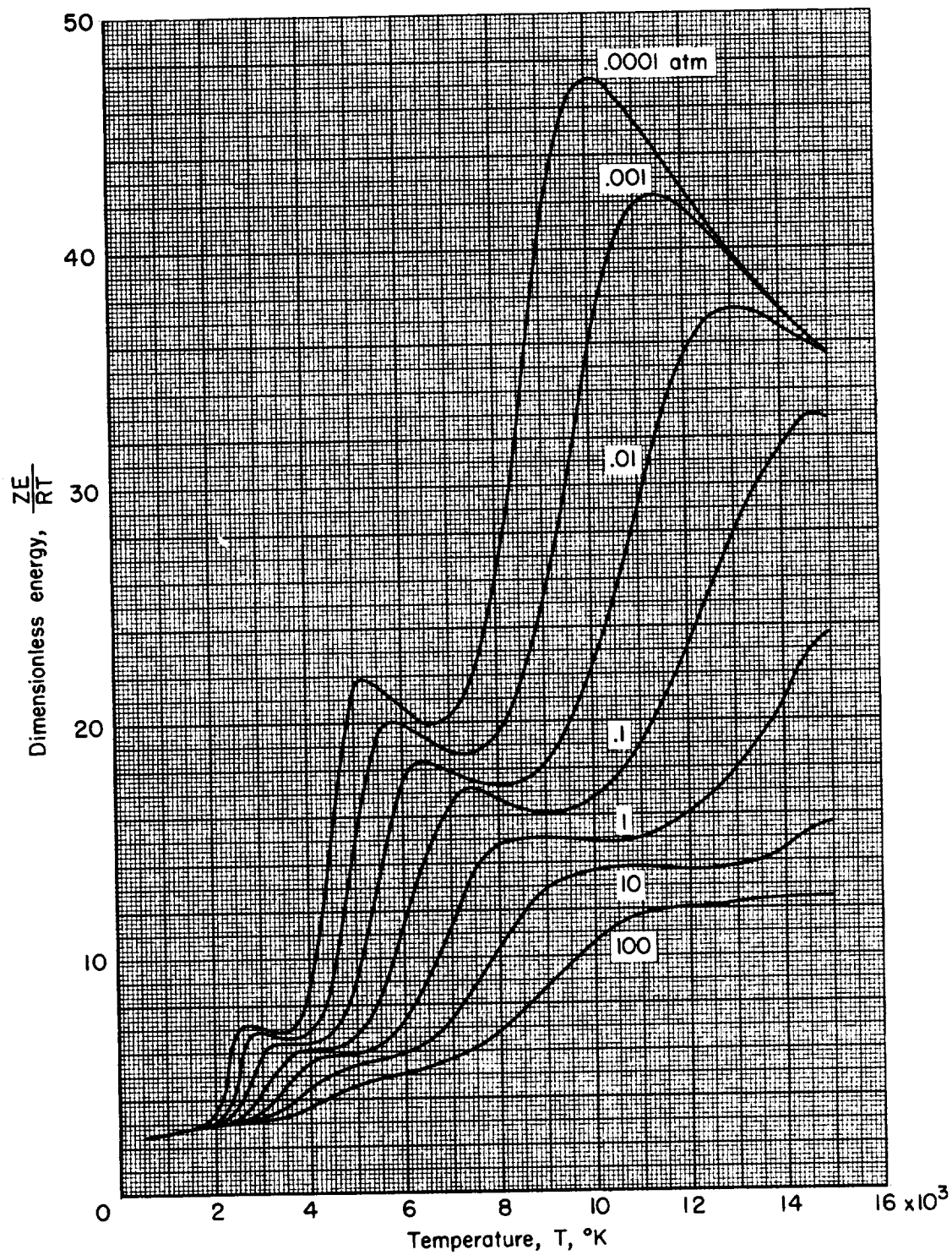
Figure 2.- Energy of air as a function of temperature.
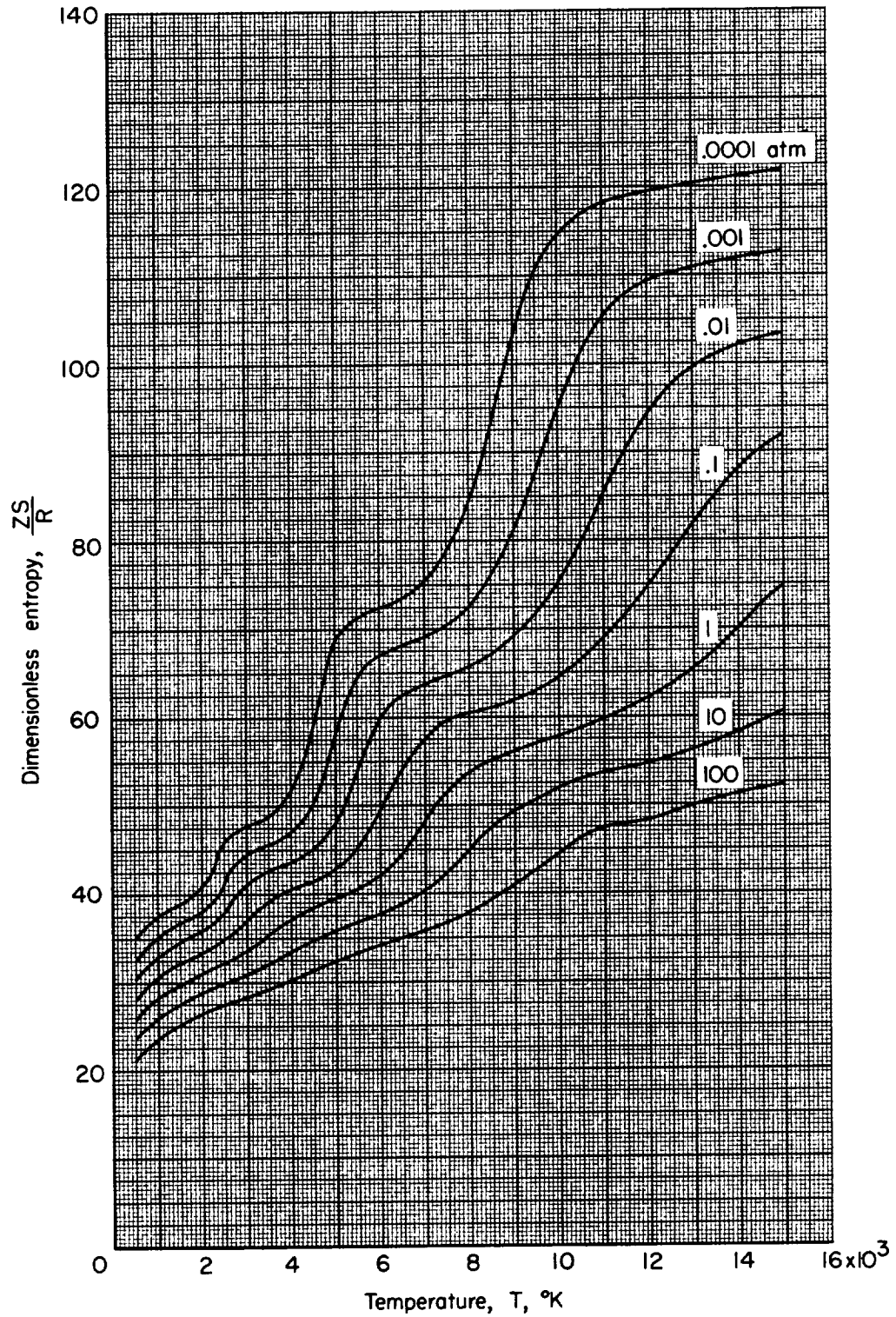
Figure 3.- Entropy of air as a function of temperature.
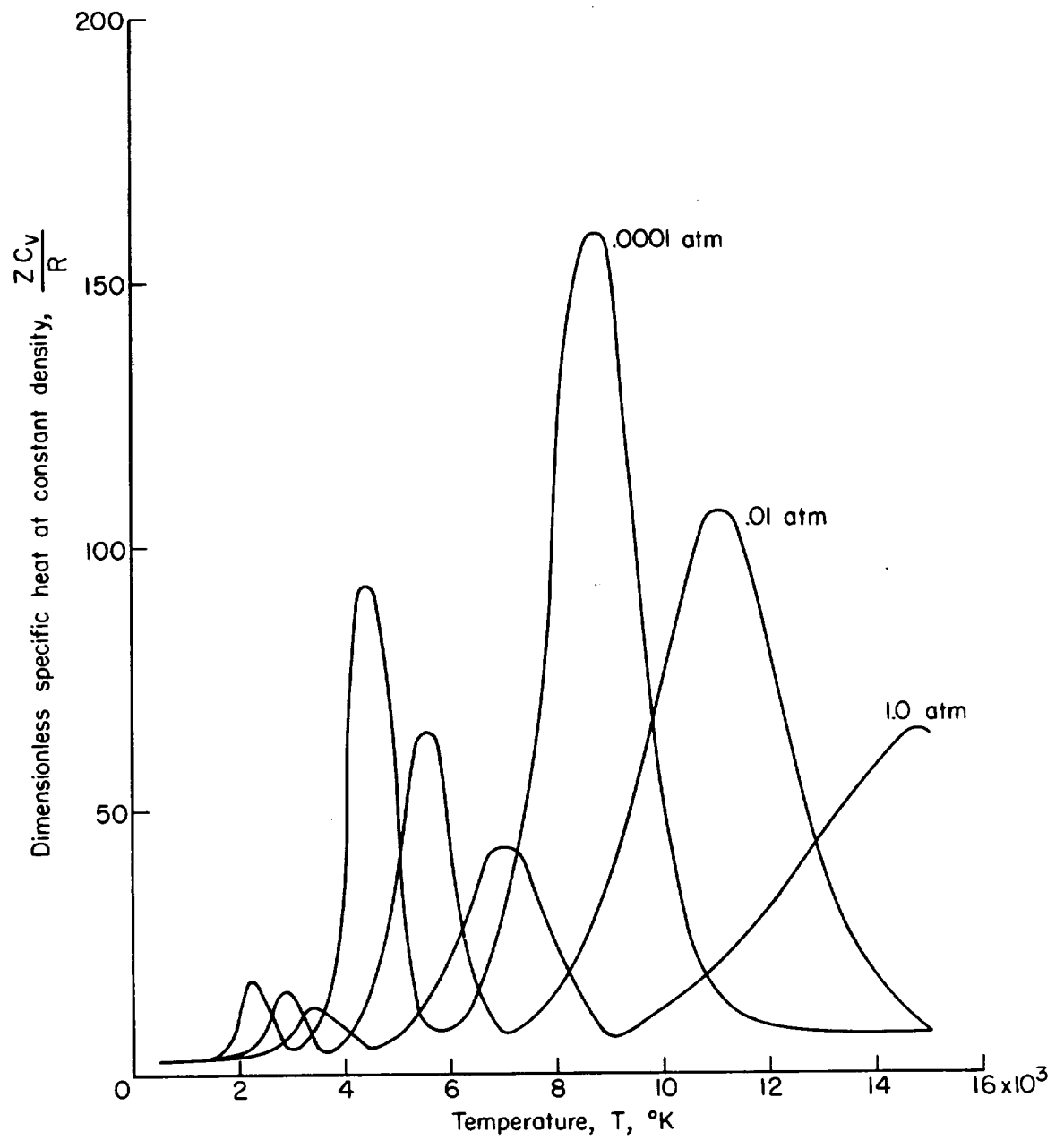
Figure 4.- Specific heat of air at constant density as a function of
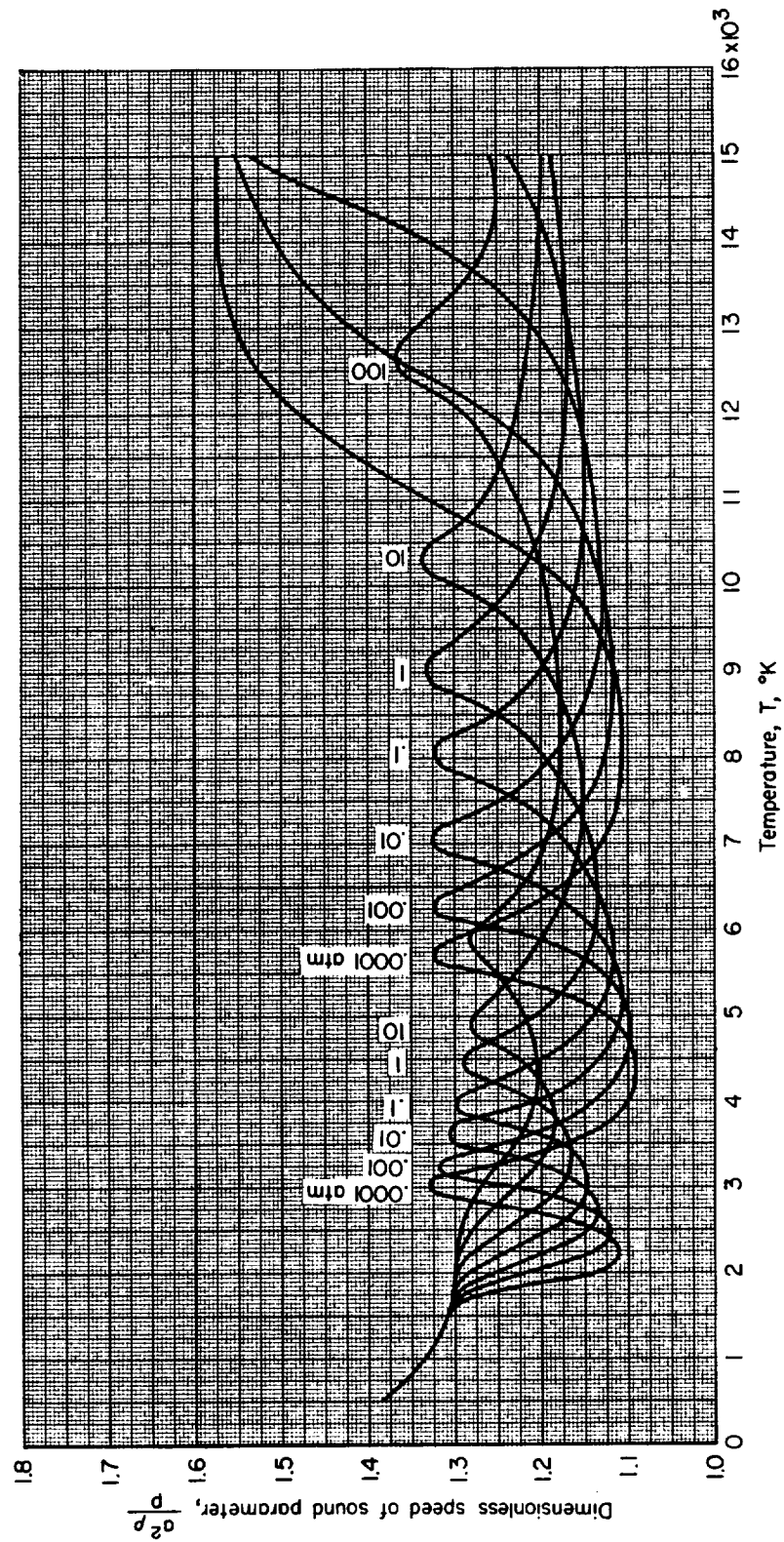temperature.

Figure 5.- Zero frequency speed of sound parameter for air as a function of temperature.
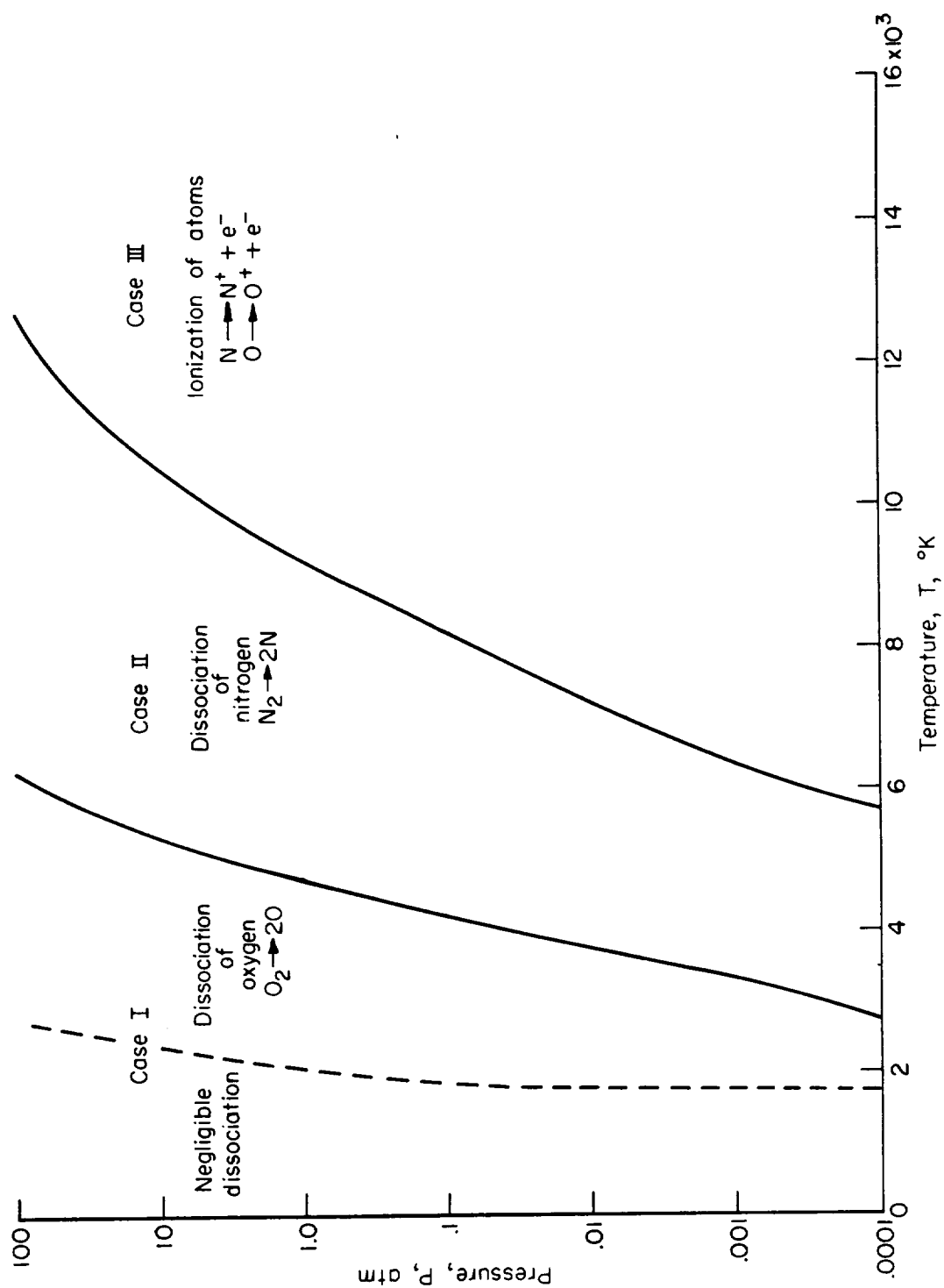
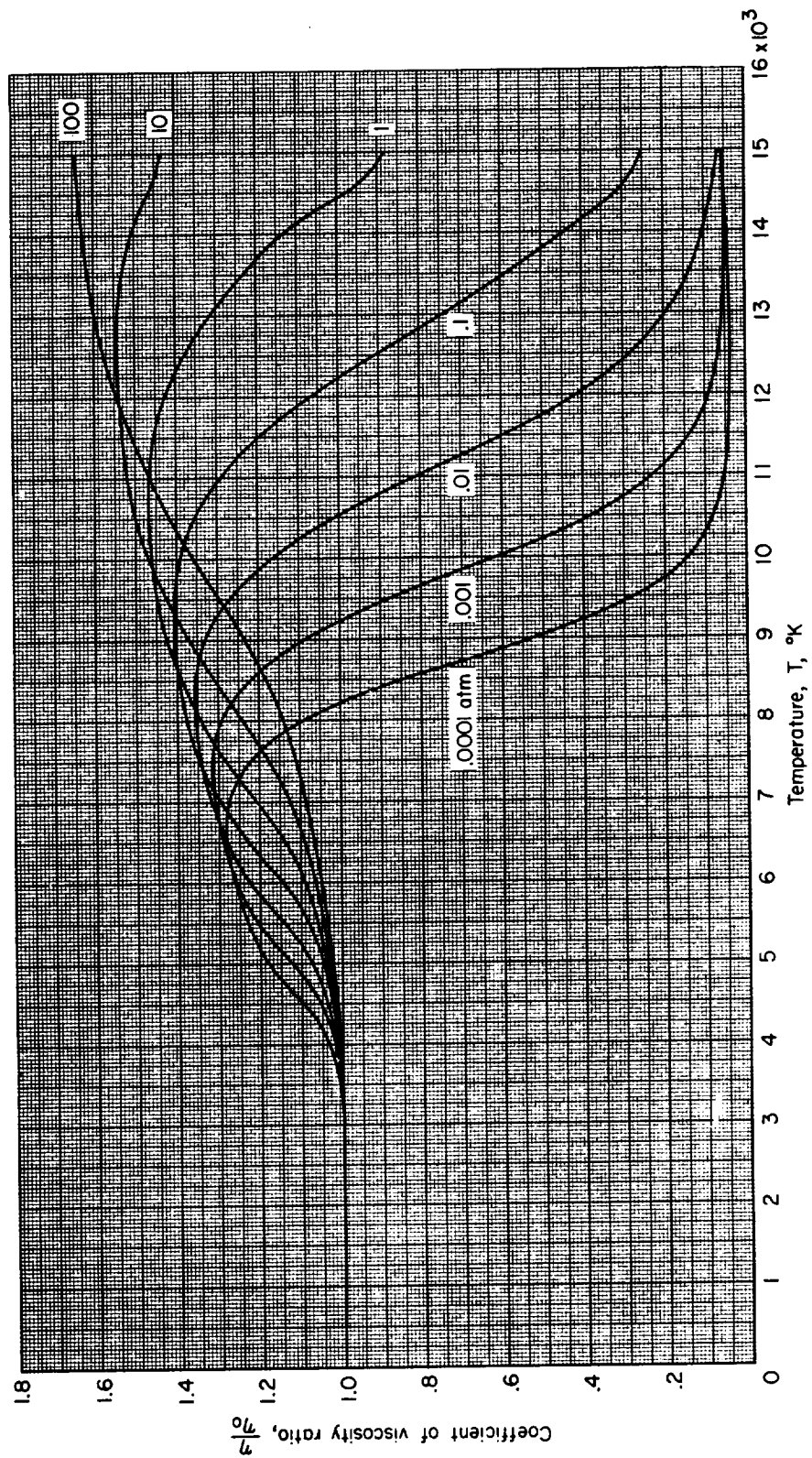Figure 6.- Domains of pressure and temperature for the major chemical reactions in air.

Figure 8.- Ratio of the coefficient of viscosity for air to the reference coefficient, η_o, as a function of temperature.
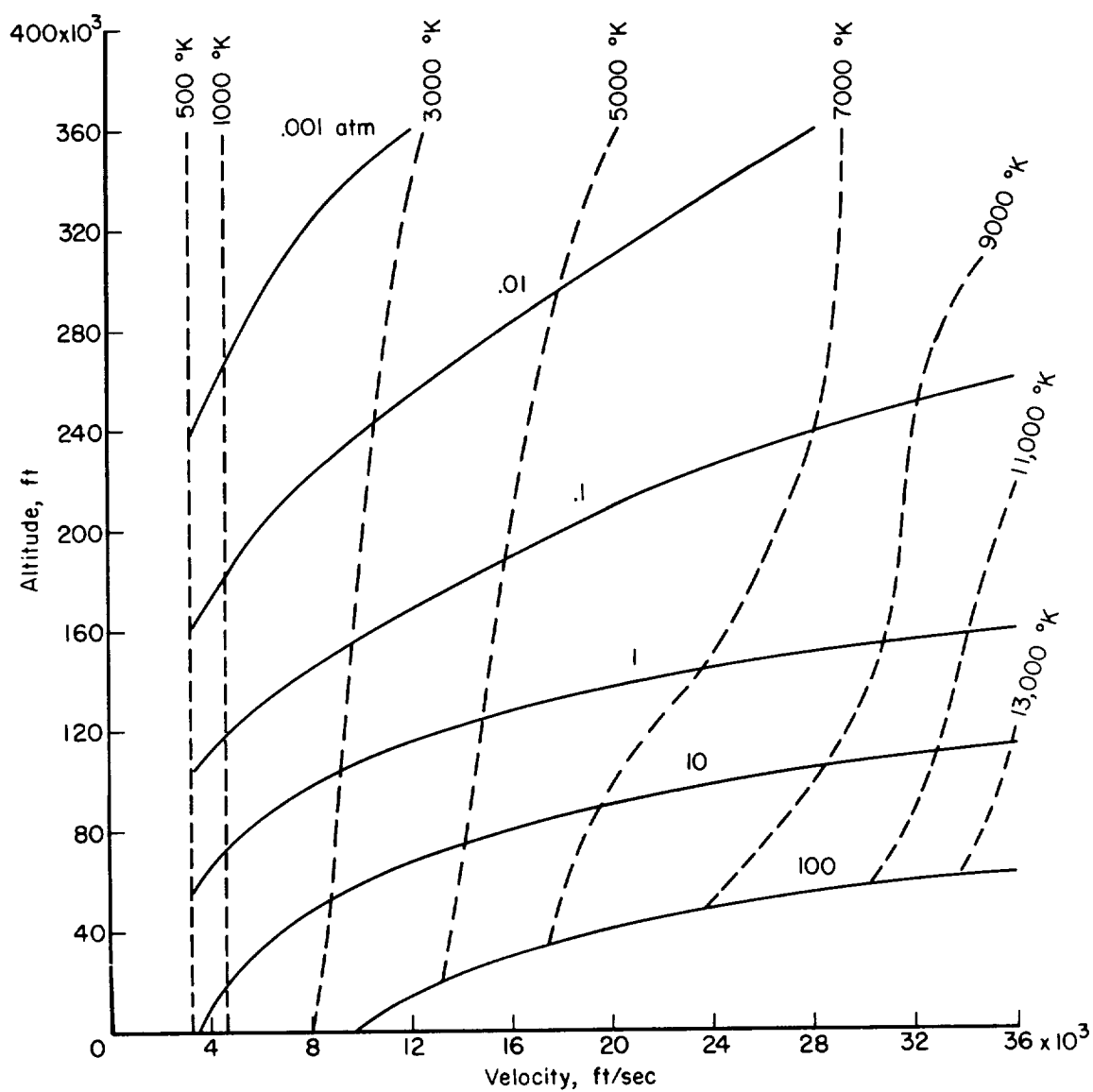
Figure 7.- Stagnation temperature and pressure in air as a function of altitude and velocity.
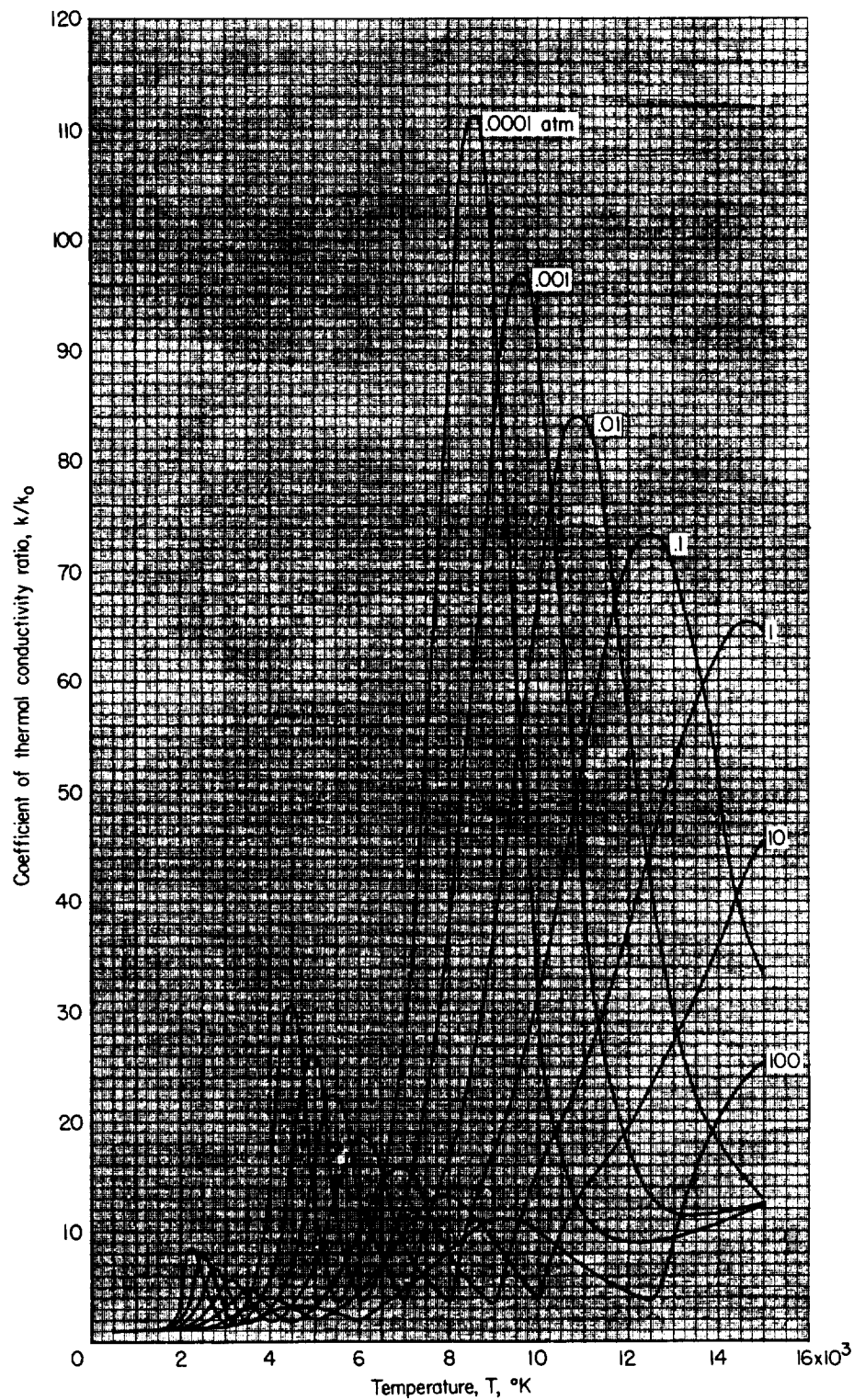
Figure 9.- Ratio of the coefficient of thermal conductivity of air to the
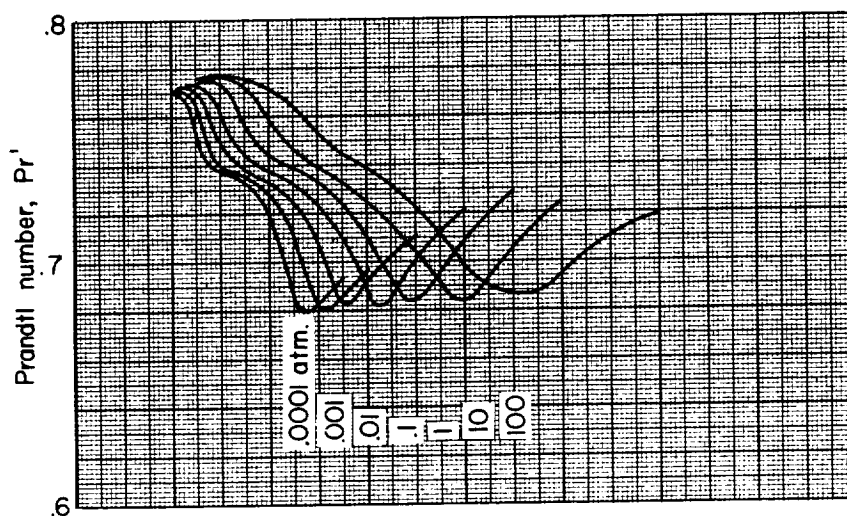reference coefficient, k_O, as a function of temperature.
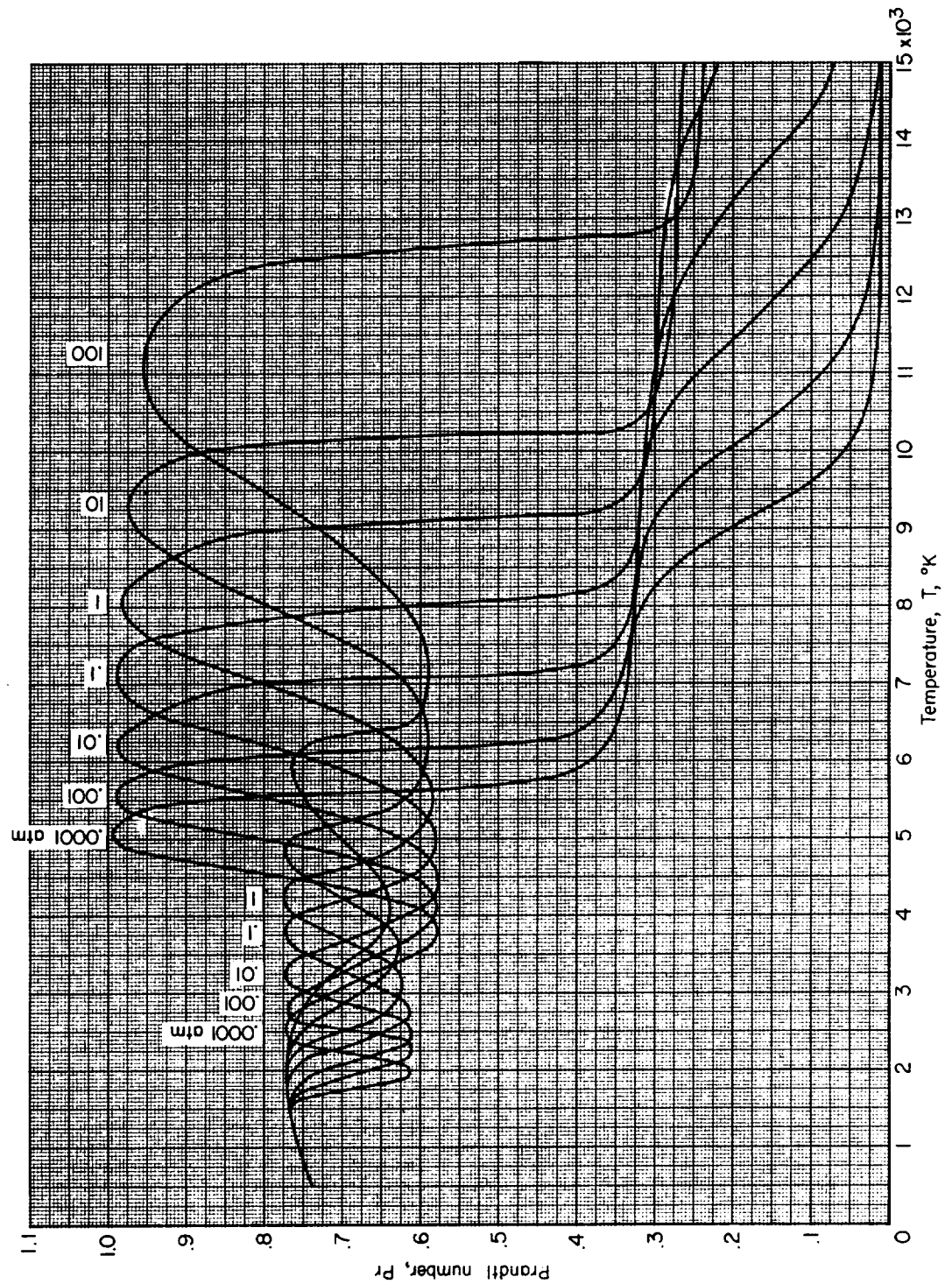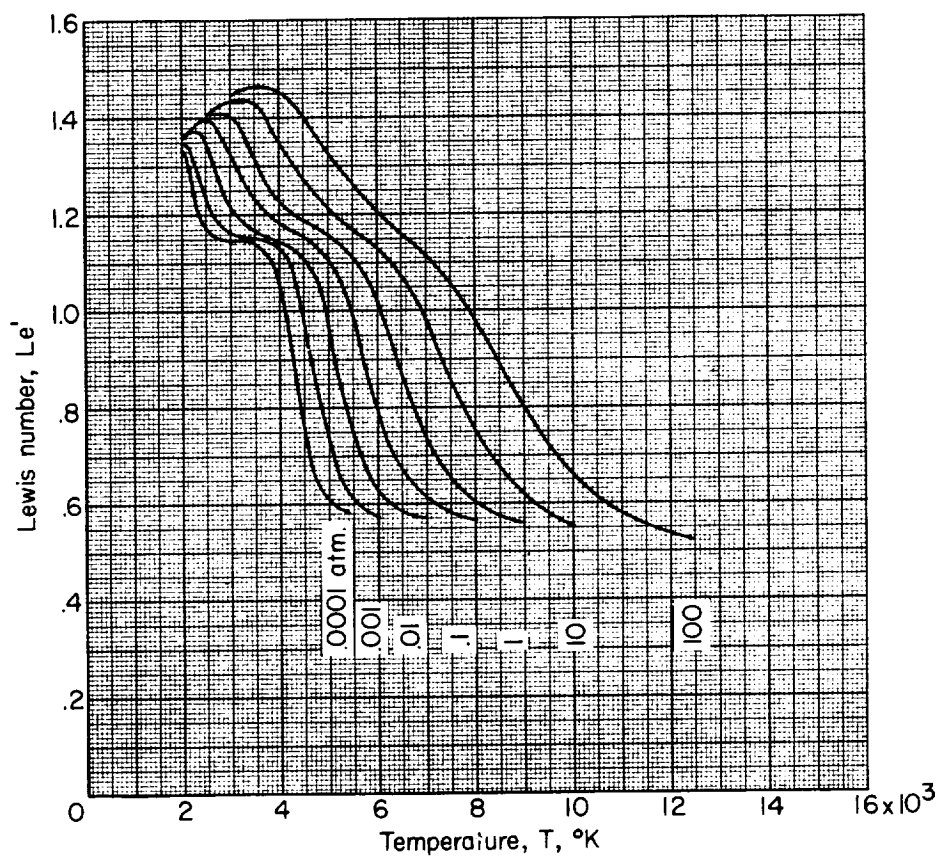
Figure 10.- Prandtl number for air as a function of temperature.

(a) Prandtl number

(b) Lewis number

Figure 11.- Partial coefficients for air as a function of temperature.